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IN ALL ITS APPLICATIONS TO

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INCREASE IN TEMPERATURE OF CELLULOSE ON ABSORPTION OF ATMOSPHERIC MOISTURE.

By CLAYTON BEADLE.

I HAVE already pointed out (*Nature*, xlix., 457) that "cellulose, when rendered anhydrous by placing it in a water-bath or desiccator, is found to rise considerably in temperature when exposed to a damp atmosphere. This may, however, be caused by the liberation of heat, due to the condensation of moisture from the gaseous state. If so, no rise in temperature would be noticed in plunging anhydrous cellulose into water." . . . "I have found that dry cellulose placed in a damp atmosphere remains at a higher temperature than its surroundings so long as it is taking up moisture, which appears to be greater when the rate of absorption is greatest. By the time it has recovered its normal condition of moisture, it has sunk to the temperature of its surroundings."

Since the above observations were made I have completed a number of experiments in this direction. These experiments, in my mind, clearly indicate that some sort of a union takes place between the cellulose and the moisture, that it assimilates, and that this union is attended by the liberation of heat.

In the following experiments the amount of heat liberated must be much greater than that indicated by the rise of temperature of the thermometer imbedded in the cellulose, since the specific heat of the thermometer is many times greater than that of the cellulose. They serve to show, however, the variations of temperature as the moisture is absorbed. Those marked with an asterisk show where air was blown against the cellulose. It will be noticed that wherever this is done the assimilation of moisture has been more rapid, and also the difference in temperature between the cellulose and surrounding air has been increased. Even when the difference has remained stationary for a short time, a blast of air will cause a further increase. I find, moreover, that the rise of temperature is greatest when the surrounding air is charged with moisture. It appears probable that the amount of moisture assimilated bears a direct relation to the heat liberated, but no conclusion can be arrived at until actual measurements of the heat liberated have been made and compared directly with the rate of absorption.

Two Grms. of Cotton-Wool Previously Dried in Air-Bath at 220° F.
(For increase in weight during absorption).

1.	2.	3.	4.	5.
0	92·85			
1	93·10	0·25	0·25	0·25
2	93·3	0·45	0·20	0·20
*3	93·7	0·85	0·40	0·40
4	93·9	1·05	0·20	0·20
5	94·2	1·35	0·30	0·30
6	94·55	1·70	0·35	0·35
7	94·75	1·90	0·20	0·20
8	95·00	2·15	0·25	0·20
10	95·35	2·50	0·35	0·18
12	95·65	2·80	0·30	0·15
17	96·20	3·35	0·55	0·11
22	96·60	3·75	0·40	0·08
*27	97·55	4·70	0·95	0·19
*32	98·15	5·30	0·60	0·12
*37	98·55	5·70	0·40	0·08
*42	98·90	6·05	0·35	0·07
47	99·05	6·20	0·15	0·03
52	99·15	6·30	0·10	0·02
62	99·15	6·30	0·00	0·00

1. Time in minutes of exposure.
2. Weight of cotton on assumption that air-dry weight equals 100.
3. Gain per cent on air-dry weight.
4. Gain since last weighing.
5. Gain per minute.

Two Grms. of Cotton-Wool Dried in Desiccator for Twenty four Hours.
(For increase of temperature during absorption).

6.	7.	8.	9.		10.
0	57·0°	57·0°	0·0		
1	57·0°	57·5	0·5	+	0·5
2	57·0°	58·0	1·0	+	0·5
3	57·0°	59·3	2·3	+	1·3
4	57·0°	60·5	3·5	+	1·2
5	57·0°	61·0	4·0	+	0·5
8	56·8°	60·5	3·7	−	0·1
*10	57·0°	60·0	3·0	−	0·35
*11	57·0°	59·7	2·7	−	0·3
18	57·3°	59·0	1·7	−	0·15
29	57·8	58·5	0·7	−	0·09
46	58·0	58·0	0·0	−	0·04

Two Grms. of Cotton-Wool Dried in Air-Bath at 220° F.
(For increase of temperature during absorption).

.	7.	8.	9.	10.
0	56·5	56·5	0·0	0·0
1	56·8	57·2	0·4	+ 0·4
2	56·5	58·0	1·5	+ 1·1
5	56·3	59·2	2·9	+ 0·5
6	56·3	59·7	3·4	+ 0·5
7	56·3	60·0	3·7	+ 0·3
8	56·3	60·2	3·9	+ 0·2
9	56·3	60·4	3·9	0·0
*10	56·3	60·7	4·4	+ 0·5
*12	56·2	60·9	4·7	+ 0·15
13	56·2	61·0	4·8	+ 0·1
15	56·6	61·4	4·8	
*16	56·6	61·6	5·0	+ 0·2
20	56·2	61·2	5·0	
26	56·0	60·8	4·8	− 0·05
31	56·0	60·0	4·0	− 0·16
39	56·2	59·3	3·1	− 0·11

6. Time of exposure in minutes.
7. Temperature of air (degrees F.).
8. Temperature of cotton (degrees F.).
9. Difference between 7 and 8.
10. Rate of increase (+) or decrease (−) of difference during interval, expressed in degrees per minute.

ACTION OF METALLIC MAGNESIUM UPON MANGANOUS SALTS.

By JOS. G. HIBBS and EDGAR F. SMITH.

The statements relating to the action of metallic magnesium upon solutions of manganous salts are contradictory; thus Manck ("Ueber d. Verh. d. Magnesium und Aluminium gegen Salzlösungen," Goettingen, 1862) states that metallic manganese is readily precipitated by magnesium from neutral solutions of manganous nitrate or chloride. Phipson (*Jahresb.*, 1864, 192) corroborates this, and remarks that the manganese separates as a regulus. The observations of Roussin (*Jahresb.*, 1866, 170), Comaille (*Comptes Rendus*, lxiii., 556; *Jahresb.*, 1866, 171), and Kern (Chemical News, xxxiii., 236), on the other hand, seem to demonstrate that metallic manganese is not thrown out of manganous salts by metallic magnesium.

We have tried the action of the last metal on manganous salt solutions, both in the presence of alcohol and ether. In using these liquids, our aim was to reduce the liability of oxidation of manganese, if any should appear, to a minimum.

Experiment 1.—In this trial magnesium acted upon aqueous manganous chloride in the presence of alcohol for a period of two hours. At the expiration of this time the liquid was distilled off, and the material remaining was then carefully analysed. 0·2582 grm. substance was used for this purpose. It showed the presence of 0·0284 grm. of chlorine, 0·1392 grm. of magnesium, and 0·0539 grm. of manganese, or a total of 0·2215 grm.

Experiment 2.—In this both ether and alcohol were added to the solution upon which the magnesium acted. After removal of the liquids the residue was dried in an atmosphere of nitrogen. 0·6530 grm. of it showed the presence of 0·0993 grm. of chlorine, 0·3059 grm. of magnesium, and 0·1865 grm. of manganese, or a total of 0·5917 grm. The action of the magnesium in this instance was only continued through one and a half hours.

Experiment 3.—The conditions here were practically the same as those in Experiment 2. The substance was dried, as there, in an atmosphere of nitrogen. Upon analysing 0·7120 grm. of the dry residue, it revealed the presence of 0·2302 grm. of chlorine, 0·2339 grm. of magnesium, and 0·1779 grm. of manganese.

In these three trials, as in others which were made, the sum total of the constituents of the reaction product, obtained by analysis, is less than the quantity of material taken for analysis, indicating that, in all probability, it is not metallic manganese which is precipitated by magnesium, but rather a hydrated oxide, as was suggested by Kern, who used a saturated solution of manganous chloride, and allowed metallic magnesium to act upon it for a period of six to eight hours, with this result—

$$3MnCl_2+3Mg+3H_2O=3MnO+3MgCl_2+3H_2,$$

and in the presence of water the manganous oxide passes into the protosesquioxide.

Metallic manganese thrown out by the electric current oxidises rapidly on momentary contact with the air, and even if it should come down as metal, through the action of magnesium, it is scarcely probable that, in the finely divided state in which it would be, it could long resist the action of the surrounding water.—*Journal of the American Chemical Society*, xvi., No. 12.

A REVOLUTION IN VOLTAIC ELECTRICITY.

The Boron Carbon Battery.

By H. N. WARREN, Research Analyst.

The numerous voltaic cells that are constantly described upon the pages of scientific literature, and after all which are so modest as regards their voltage, naturally suggest an apology to offer yet another. The above title is not, however, too ambitious, when I may mention that after a lengthy and troublesome research I have had the satisfaction of arranging a battery capable of producing 3 volts and giving a constant current from 2 to 2·5 for almost unlimited duration. Such a battery may be in some measure approached by either Bunsen or Grove's cell; but in mine there is a complete absence of fuming acid, and it costs less than one penny for ten hours' action. The cells themselves are constructed upon the flat system, with sliding carbon plates enclosed in teak-wood boxes, the carbons being chemically prepared by special treatment, whereby gaseous compounds of boron are so decomposed as to allow of the boron becoming absorbed into the pores of the carbon, which are afterwards soaked in solution of oxalate of platinum, and heated to redness in an atmosphere of hydrogen. A flat porous cell encloses the zinc element, while the outer cell contains a specially prepared manganic salt in admixture with other substances.

The cells are for several reasons arranged in a series of three, and thus readily constructed for voltage or quantity, and complete up to 50 ampères, the cost at the commencement being no greater than batteries that afford only half the power.

As illustrative of the power of these particular cells, twelve small ones were arranged in a series, the arc produced between the carbon points being more than the naked eye could bear. Over two feet of platinum wire was raised to incandescence, whilst the heat from the arc produced readily fused titanium, chromium, and tungsten, and volatilised platinum in quantity. A series of fifty of most batteries would have failed to have accomplished it. As a lighting agent for large or small lamps they stand unrivalled, whilst the absence of fumes allow of their presence in dwellings, conservatories, or places of a like nature. For driving motors one cell is usually sufficient, while, on the other hand, for electro-chemical demonstration three cells will be found sufficient for the entire work of a large laboratory.

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THE ATOMIC AND MOLECULAR SOLUTION-VOLUME.

By J. TRAUBE.

In connection with earlier communications I determined the specific gravities of a great number of solutions of salts—especially aqueous—by the pyknometric method. The directions given in my guide to "Physikalisch-chemische Methodon" (Physico-chemical Methods) were closely adhered to, and care was taken for the purity of the preparations.

These determinations of specific weights served for the calculation of the following values.

Let *m* be the molecular weight of a substance dissolved in water, *e.g.*, the quantity of water which is contained in the solution for each mol. of the dissolved substance; *d*, the density of the solution referred to 4°; δ, the density of water as such. I then call the constant—

$$Vm = \frac{m + aq}{\alpha} - \frac{aq}{\delta},$$

the *molecular solution-volume* of the dissolved substance and the corresponding constant $V\alpha$ the *atomic solution-volume.*

The atomic and molecular solution-volumes would be equal to the atomic and molecular volumes of the dissolved substance if the density of the water as such were equal to the density of the water in the solution. On this in the sequel.

The molecular solution-volume is, in the first place, in the closest relation to the degree of electrolytic dissociation, or, as I shall call it, the degree of ionisation of the dissolved substances.

I still adhere to my former views as to the nature of ionisation, and I believe that the assumption of a far-reaching loosening of the ions in the dissolved mol. of an electrolyte agrees better with the facts than the assumption of complete disintegration of the molecule.

Whether, however, we select the point of view of the hypothesis of ionisation, or that of the electrolytic dissociation, is indifferent, but in any case either ionisation or electrolytic dissociation must be considered in calculating the molecular solution-volume. This done, only solutions of equal degree of ionisation were compared with each other, and where it was necessary observations of the congelation-point were effected.

In this manner numerous combinations of altogether 50 elements were compared together, and a series of simple relations of the atomic molecular solution-volumes were established.

A fuller account of this investigation will be given in the *Zeit. für Anorgan. Chemie.*

A comparison of the molecular solution-volumes of corresponding compounds leads to the following proposition.

The elements hydrogen, lithium, sodium, monovalent copper, silver, monovalent gold, and monovalent mercury have an equal atomic solution-volume.

In the series sodium, potassium, rubidium, cæsium, the atomic solution-volume increases with increasing atomic weight by a mean of 10 units of its value. The atomic solution-volume of rubidium is equal to that of ammonium.

Thallium compounds have a generally molecular solution-volume greater by some units than the corresponding potassium compounds.

The elements calcium, strontium, and lead have an equal or approximately equal solution-volume, also the elements zinc and magnesium, barium and cadmium, divalent iron and manganese, as also nickel and divalent copper.

Barium and cadmium have a decidedly greater atomic solution-volume than the first members of the corresponding triads. The volume of red cobalt is considerably greater than that of nickel. Glucinum has among the above divalent elements the highest atomic solution-volume.

The atomic solution-volume of trivalent iron seems equal to that of aluminium; the constant of chromium is apparently rather smaller.

The *green* chromium compounds have a decidedly smaller solution-volume than the violet compounds of the same metal.

Molybdenum and tungsten have an equal atomic solution-volume (molybdates, tungstates).

In the series of the non-metals there appeared the following regularities:—

Chlorine and bromine (in the chlorates and bromates) have an equal atomic solution-volume. Iodine (in the iodates) has a volume smaller by about 8·5 units. In the chlorides, bromides, and iodides, the molecular solution-volume of Cl : Br : I increases by 7·5 or 10 units.

The molecular solution-volumes of the perchlorates and permanganates are equal.

The atomic solution-volume of fluorine is smaller than that of chlorine by 16 units.

The same difference appears again for oxygen—sulphur, nitrogen—phosphorus.

In the series, sulphur, selenium, tellurium, phosphorus, arsenic, antimony, silicon, titanium, zirconium, the atomic solution-volume increases with the increasing atomic weight. The differences amount to 7—9 units. Equal atomic solution-volumes appears in nitrogen and vanadium (nitrates, vanadiates), carbon and silicon (carbonates and silicates).

These are the most important regularities which have hitherto appeared.

Such compounds, however, have been left out of consideration in this exposition which are formed by the sole combination of kindred elements, *i.e.*, such as stand near each other in the series of electro-chemical tensions. For such compounds, and for the elements themselves, other relations come into force.

The difference of the molecular solution-volumes of $K_2SeO_3 - K2SO_3$; $K_2SeO_4 - K_2SO_4$ was as a mean $= 7·5$. On the contrary, instead of this increase a decrease of 10 units was determined from sulphur to selenium for aqueous solutions of sulphurous and selenious acids. The difference $KBr - KCl$ was $= 7·5$; $CaBr_2 - CaCl_2 =$ about 2·75; $AlBr_3 - AlCl_3 = 3·75$. On the contrary, this difference for $PBr_3 - PCl_3$ was = about 2 units. The circumstance that the determinations here were effected in benzene did not come into consideration. Quite corresponding results were reached for the series phosphorus, arsenic, antimony, as also carbon and silicon, on a comparison of the chlorides.

It seems that for the combinations of electro-negative elements with each other there appear quite different volume relations than for the compounds of electro-negative with electro-positive elements.

The regularities observed hold good, as my experiments and calculations have shown, for the most different temperatures and solvents.

In dissolved substances in the state of dilute solutions, crystalline water can be assumed either not at all or only exceptionally. In this respect I must modify a view which I have hitherto expressed. The molecular solution-volume is a strictly additive constant.

The difference Ag_2SO_4—Na_2SO_4—K_2SO_4 is very approximately equal to that of all other silver, sodium, and potassium compounds, the differences K—½Mg—½Sr—½Ba, &c., are in all corresponding compounds equal, or approximately equal, so that we are justified in establishing the following proposition:—For similar degrees of ionisation of a dissolved substance the influence exerted by a given ion upon the value of molecular solution-volume is approximately equal and independent of the other ion which is present with it in solution.

Most important is the question as to the relation of the atomic and molecular solution-volumes to the atomic and molecular volumes of the dissolved substances.

We can approach more nearly to this question if we compare the differences of the molecular-solution volumes with the differences of the molecular-solution volumes calculated for the solid or the liquid state.

It appears that wherever regularities for the values of the molecular volume are established, the same differences may be calculated as for the molecular solution-volumes of the dissolved substances. That which is the *rule* for solid bodies or homogeneous liquids, is for dilute solutions the *law*. This is a theorem the significance of which will appear also in properties other than the molecular solution-volume, *e.g.*, the index of refraction.

The difference $\Delta\,vm$ for $K-Na$ is calculated for the dissolved condition generally as on an average = 10; the same difference reappears in a large number of potassium and sodium salts on comparing the molecular volumes of the solid compounds.

As for the dissolved condition in general, the difference in the solid state is in a number of cases $Ag-Na=0$, likewise $Pb-Ca-Sr$; $Mg-Zn$; $Mo-W$; also NO_3-Cl, $I-Br=10$; $Br-Cl=7{\cdot}5$, &c.

We cannot wonder that for the solid state there are only found regularities.

Disturbing influences come here into consideration.

The defectiveness of the determinations of the specific gravities; the circumstance that a body may have different specific gravities; the aggregation of molecules to greater complexes; the alteration of the specific gravities by crystalline water, and perhaps also the inaccurate selection of the temperatures of comparison. In consideration of these points it follows that the differences of the molecular solution-volumes are, in fact, to be regarded as the differences of the true molecular volumes, and that all the regularities deduced for the molecular and atomic solution-volumes are valid also for the molecular and atomic volumes.

That the values of the molecular solution-volume as such are not equal to the values of the molecular volumes of the dissolved substances follows from the circumstance that many of these values are vanishingly small and frequently even negative, at least at certain temperatures and in certain solvents. My earlier assumption of reducing negative character of the values to the formation of hydrates, I have been compelled to reject on account of the purely additive relation of the molecular solution-volume. Hence nothing is left but, in all such cases, to admit a contraction of the total water. That certain ions effect such a contraction, but others not, is *à priori* improbable; I incline therefore to the view that in all cases there occurs an attraction of water on the part of the dissolved ions the rather that such an assumption seems required for the total region of the organic substances.

As now in many cases, and especially on comparing kindred substances, the differences of molecular solution-volumes and molecular volumes are equal to each other, there follows the proposition:—Kindred ions exert, no matter with what other ions they are conjointly present in the solution, an equal attraction upon the solvent.

This proposition, which, in consideration of the above-mentioned disturbing influence in the determination of the molecular volume, may probably be generalised, extended to all ions and non-ionised molecules, seems to me of no small importance for the theory of osmotic pressure and of electrolytic dissociation. I purpose shortly returning to it in an especial memoir.

An Elementary Atom may occüpy Different Spaces.

I call this property the *polysterism* of the elements.

A change of space occurs in most processes of reduction and oxidation, in the separations and the solutions of many metals, in processes of neutralisation, and wherever compounds of elements electro-chemically adjacent to each other pass into compounds of elements which occupy respectively remote places in the series of tension.

Polysterism is therefore important in the first place in various departments of chemical energetics, especially for thermo-chemistry and electro-chemistry.

Polysterism further takes us a step onwards in the theory of valence. The varying valence of an elementary atom is generally connected with a change of the atomic volume. This alteration of the state of the atom presents the possibility of understanding the non-constancy of the valence.

Occasionally polysterism becomes prominent without connection with any alteration of the valence. The change of colour of the chromium salts may be referred hither. I am also inclined to interpret the colour-phenomena of the cobalt salts and copper chloride in the same manner.

How far polysterism is otherwise of importance in deciding questions of isomerism must appear from future researches. The question must especially be raised if carbon is polysteric.

The regularities for molecular and atomic volumes observed are intimately connected with the isomorphism of the compounds; molecular volume and isomorphism more closely connected than it has been hitherto assumed. The small variations of molecular volume run in most cases parallel with the changes of form. The natural families of the elements which result on the basis of the relations of the molecular volumes generally coincide with the families which are established from the consideration of the crystalline forms. See the chapter on "Isomorphism," by Arzruni, in Landolt's new edition of Graham-Otto's text-book.

It must lastly be shown that the regularities here demonstrated demand attention, in as far as they in so many cases admit of calculations of specific gravities, sometimes of such accuracy that the calculation is preferable to observation. They are of value also as a check on the specific gravities of solutions hitherto published. The molecular solution-volumes often explain various phenomena of solution, such as decomposition, formation of double salts, &c.

I propose to determine the molecular solution-volumes of organic substances, and I may already mention that here also the regularities for homogeneous substances discovered by Kopp appear far closer on observing the dilute solutions. A similar fact may certainly be expected for the indices of refraction. — *Berichte Deutsch. Chem. Gesellschaft*, xxvii., No. 18, p. 3173.

A CONSTANT ERROR IN THE DETERMINATION OF NITROGEN IN ORGANIC SUBSTANCES BY WEIGHING THE METALLIC PLATINUM REMAINING AFTER THE IGNITION OF AMMONIUM-PLATINO-CHLORIDE.

By Prof. Dr. L. L. de KONINCK.

The results obtained in the analysis are never calculated from the weight in vacuo, and to do this is, as a rule, needless, since the error arising = O if the material under analysis and the substance by the weighing of which the result is obtained have the same specific gravity. In most cases in practice we approach this condition sufficiently closely, so that the error occasioned may be disregarded. It is otherwise in the determination of nitrogen in organic substances, and even, though to a less extent, in ammoniacal salts and nitrates, if the proportion of nitrogen is found by weighing the platinum remaining from the ammonium platino-chloride.

Assuming that the specific gravity of the substance in question is 1·20, the true weight will be equal to this weight + the weight of the air displaced by the substance, and if we take the weight of a litre of air under the conditions prevalent at the time of weighing as 1·2 grms., the proportion of the real to the apparent weight will be 1·001 : 1·000. For platinum which has the specific gravity 21·5, the true weight approaches more closely to that found, and would correspond to the number obtained by multiplying the apparent weight by 1·00006. If we call the apparent weight of the substance as weighed in air P, and the weight of the platinum determined under the same conditions and remaining on igniting the ammonium platino-chloride as p, the proportion between platinum and the substance employed would be p/P, and would in reality be written as—

$$\frac{p \times 1{\cdot}00006}{P \times 1{\cdot}00100}.$$

According to this calculation the difference would amount to—

$$\frac{p}{P} \times 0{\cdot}00094,$$

or about 0·001, corresponding to an approximate quantity of 0·1 per cent. For a substance containing 10·0 per cent nitrogen we should find 10·01 per cent. This error is not considerable, but it requires to be taken into account when comparing the results obtained by different methods. An exact result can be obtained in such cases by deducting 0·1 from the percentage found.—*Chemiker Zeitung*.

THE DISTRIBUTION OF THE ORGANIC ELEMENTS.*

By Prof. W. PREYER, M.D., Ph.D.

The small number of the organic elements constantly excites anew the wonder of the naturalist. Only one-fifth part of all the known elements serves for the formation and the life of all animal, vegetable, and protistic beings, whether they are developed or rudimentary, healthy or diseased, great or small, common or rare. The compounds of merely 14 elements suffice for maintaining the entire immense fulness of life on the earth's surface. There are few facts which equally excite the wonder of the beholder of the inexhaustibility of the resources of living nature. It is certainly worth our while to consider the distribution and the properties of those privileged simple bodies, especially as it fosters our hope of throwing light from a new side into the obscurity of the greatest riddle—the mystery of life.

Firstly, the number of the organic elements. It is certain that from animals nothing can be obtained other than from plants, since the former are supported by the latter. All animals are either carnivorous or herbivorous, or both, *i.e.*, omnivorous; the carnivora feed upon the herbivora, so that ultimately all animals without exception feed from the vegetable world. The food of plants, contained in the air, the water, and the soil, must contain the same elements as the tissues of the plants themselves, since from the unchangeable character of every chemical element on the earth's surface nothing new can be produced.

Hence follows of absolute necessity that all the elements required for the support of animals—man included—must be contained in the food of plants. In fact during the last three decennia numerous and careful experiments have confirmed this weighty conclusion more and more firmly.

Many plants can grow, bloom, and fructify, if along with the ordinary atmospheric air they are supplied with a nutritive liquid containing water, saltpetre, gypsum, common salt, magnesium sulphate, calcium phosphate, along with traces of some soluble compound of iron, and traces of silicate and a fluoride.

Hence are, in fact, united all the organic elements and the compounds of the widest distribution. Paradoxical as it may sound, it is still true that the elements of these few compounds of the modest diet of plants are exactly the same as those of man's most sumptuous banquets. Again, we find these same elements in that nutriment which we all exclusively receive in the beginning of our life, *i.e.*, in milk. This alone, in truth the only complete food, is capable of supplying to the human body in its early development all the material required for its life, and in the most suitable form, just as the salts in the nutritive liquid of plants supply to it what it needs.

Entirely as plant-food differs from milk, or, indeed, from any human food, the elements of both are the same, in kind and number, as those of the maternal body producing the milk and that of the child, namely:—(1) Carbon, which the higher plants derive from the carbonic acid of the air. This carbonic acid they decompose under the action of solar light by means of the chlorophyll in their cells, and exhale at the same time oxygen. (2) Oxygen. This also is obtained by the plant from the air and from water, and at the same time (3) Hydrogen. There follows (4) Nitrogen; which plants chiefly obtain from saltpetre, *i.e.*, the nitrates of the alkaline metals, and also from ammonia. (5) Sulphur, which is obtained by the roots by decomposing the sulphates in the soil, namely, the sulphates of the alkaline and earthly-alkaline metals. (6) Phosphorus, derived from the alkaline and earthly phosphates. (7) Chlorine, required by many plants only in extremely small quantities, is obtained from potassium and sodium chlorides. (8, 9, 10, 11) Calcium, magnesium, potassium, and sodium, the last only in very minimum quantities, are supplied to plants of the soil in which they grow in the state of nitrates, phosphates, sulphates, and chlorides. (12) Iron, is supplied in water as carbonate, and perhaps as phosphate. Lastly (13), silicon is present in silicates and sand, and (14) fluorine in calcium fluoride and in the soluble alkaline fluorides.

Herewith the list of the universally distributed organic elements is exhausted. More than fourteen are not needed to form the nutriment of plants, and consequently that of animals. As both can contain nothing which is not introduced by the air inhaled and the food ingested, the above small catalogue includes all the indispensable organic elements. In them is bound up all bodily and spiritual life.

Meantime, a proposition of such scope requires other proofs before it can be fully accepted. Every given plant or animal, the diminutive egg of a parasite as well as the gigantic whale, a microscopic fungus as well as the tree to whose stem it adheres, a worm as well as a man, yield on chemical analysis always the above fourteen elements. These have truly so fundamental a significance for life, that where life is not one of them may be absent. Yet more; if the organism requires to maintain its vital activity in every direction, only the above fourteen elements—certainly in ever-varying combinations — no fifteenth or sixteenth can occur with equal universality.

What is the fruit of the empirical scrutiny? It is found in the first place that for ten of those fourteen elements their existence in every living being is placed beyond all doubt, namely, for carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, calcium, magnesium, potassium, and iron.

It is easy to demonstrate at any moment that every part of a living body contains carbon. If we dry and heat it, it blackens and is carbonised. The blackness is simply carbon, since if burnt alone in oxygen it yields only carbonic acid.

Hydrogen and oxygen must be present in mass in every living being, because each consists of water to two-thirds or four-fifths, or even nine-tenths. *Corpora non vivunt nisi humida.*

Nitrogen and sulphur are present without exception

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* A Discourse delivered before the General Meeting of the Nassau Association for Natural Science, at Wiesbaden, December 10th, 1893

since albumen contains both these elements, and there is no living tissue without albumen.

Phosphorus, calcium, magnesium, potassium, iron are always found in the ash of a plant or of the carcase of an animal, often most conveniently by means of the spectroscope.

All this is unquestionable. But in order to be sure of the presence of every such element in every plant we must not take too small a quantity for incineration, as otherwise the traces of iron might escape recognition.

Now for the four remaining elements. It has long been known that chlorine and sodium are present in every animal. Some botanists deny their presence in the higher plants. But whenever sufficient quantities of vegetable matter are burnt sodium chloride is found on the ash, even in parts remote from the sea.

The same applies to silicon and fluorine. Many plants flourish in nutrient liquids to which neither silicates nor fluorides have been added. But it does not follow that traces of these elements have not been introduced along with the other ingredients, or from the glass.

When I maintain that silicon and fluorine rank among the indispensable elements, I depend on the fact that fluorine occurs in the teeth, the bones, and the milk, and is one of the most widely distributed elements in the soil. Silica is always found in the ashes after the incineration of animal and vegetable matter.

(To be continued).

DETECTION OF SMALL QUANTITIES OF METALLIC SULPHIDES IN PRECIPITATED SULPHUR.

By R. FRESENIUS.

When in qualitative analyses a portion of the solution of a metallic salt acidified with hydrochloric acid and precipitated with sulphuretted hydrogen gives a white precipitate of sulphur, it is then permissible, in analyses where merely the detection of the metals is required, to infer the absence of metals of the fifth group (bismuth, cadmium, &c.) and such of the sixth group (arsenic, tin, &c). In accurate analyses such an analysis is not admissible, since the colour of very small quantities of cadmium, arsenic, and tin sulphide may be entirely masked by the joint presence of sulphur.

Such is the case if a coloured precipitate obtained with sulphuretted hydrogen from a solution acidified with hydrochloric acid is heated with ammonium sulphide or sodium sulphide, and a portion of the filtrate after dilution with water is mixed with hydrochloric acid. Here the white colour of the precipitate allows us to conclude the absence of large quantities of arsenic or tin, but very small quantities may still be present.

In the first or the second case it was therefore necessary in accurate analysis to wash out the precipitate, to treat it with one of the oxidising agents which dissolve metallic sulphides (hydrobromic acid, sodium peroxide, or the like), and to test the filtrate again with sulphuretted hydrogen after appropriate treatment, or to proceed with the precipitate as if it had been coloured.

The use of these circumstantial methods can in general be avoided in the following very simple manner.

A portion of the liquid containing the deposited sulphur is put in a small test-tube so as to occupy one-half. It is then covered with a layer of benzene or petroleum ether, about 2 c.m. in depth, closed with the thumb and shaken very strongly for one minute, and allowed to stand for a minute. If the white precipitate consisted merely of sulphur, it will have been dissolved in the benzene or petroleum ether, and we obtain two strata, the upper clear as water, and the lower slightly turbid. But if traces of a metallic sulphide were mixed with the sulphur they appear in the form of thin coloured films at the surface of contact of both layers, and the metallic sulphides which have remained undissolved generally coat the upper part of the test-tube above the level of the liquid with a slight faintly-coloured pellicle.

Only if such deposits are perceptible will it become necessary to have recourse to one of the two above-mentioned methods. In many cases it will be preferable to treat a larger part of the liquid in question like the small specimen just referred to, and to examine the sulphides. In this case, after the sulphur has subsided in the benzene or the petroleum ether, we filter through a wet filter, allow the aqueous solution to run off entirely, pour away the benzene or petroleum ether from the metallic sulphides which chiefly adhere to the filter, wash them with water.

I said above that my rapid process is in general available, because there are deposits of sulphur which do not dissolve in benzene or petroleum ether. Such are never obtained on adding hydrochloric acid to ammonium sulphide or sodium sulphide containing polysulphides, and very exceptionally on passing sulphuretted hydrogen into acid solutions, *e.g.*, on adding sulphuretted hydrogen to a liquid containing sulphurous or nitrous acid.—*Zeit. fur Anal. Chemie.*

ON SEPARATION OF METALS IN ALKALINE SOLUTION OF HYDROGEN PEROXIDE.

By P. JANNASCH and E. ROSE.

Separation of Bismuth and Zinc.

As initial material we used pure metallic bismuth and zinc. The amorphous zinc sulphate of commerce was found less useful, since, if dried in the air, or on long keeping, especially in summer, it lost water rapidly, and frequently gave too high results. The weighed quantities of the metals (from 0·3 to 0·45 grm. each) were covered with a little water and about 10 c.c. of strong nitric acid in a capacious porcelain capsule fitted with a handle. The solution obtained on heating was evaporated down and taken up again with 5 c.c. concentrated nitric acid and 50 c.c. of water. In another capsule we prepared at the same time a mixture of 25 c.c. of hydrogen peroxide at 3 to 4 per cent and 15 c.c. concentrated ammonia, and poured the zinc and bismuth solution, with constant stirring, into the alkaline oxidising liquid. It is quite essential to effect the precipitation in this manner, *i.e.*, in presence of a constant excess of ammonia. If this is not the case, as it would occur at first, if we poured the ammoniacal solution of hydrogen peroxide into the metallic solution, the precipitate of bismuth formed re-dissolves in the residual acid with a great loss of oxygen, and we have therefore at the conclusion of the precipitation no certain guarantee that we have really employed a sufficient excess of hydrogen peroxide. Further, after the neutralisation of the originally acid solution, the zinc will also be deposited at the same time, and only dissolves subsequently in the excess of ammonia, which, however, takes place slowly and imperfectly. These circumstances, which are opposed to an accurate separation, may be much more successfully avoided by the procedure above directed. The yellowish-grey flocculent precipitate produced (bismuth hydroperoxide) falls immediately to the bottom. After repeated stirring it is collected on a filter and washed at first with very dilute ammonia, and then with cold water, until a drop of the washings leaves no residue on evaporation. We then dissolved the precipitate on the filter with dilute nitric acid (1 : 4), using at most 10 c.c. of the acid measured, when concentrated, and the precipitation of the bismuth was repeated under the same conditions. For an ordinary analysis a single precipitation of the bismuth is sufficient, since the zinc is precipitated only in minimum traces which lie decidedly within the permissible limits of error. The precipitate of bismuth after filtration and washing was dried completely at from 90°—100°. It was then detached as completely as possible from the filter, which is cut carefully up into small pieces and transferred to a platinum crucible. This is then covered over and placed in a nickel beaker, which is also covered with an asbestos capsule, in order thus to effect a gradual incineration of the organic substance. Heat is applied by means of a so-called sieve-burner (Fletcher's pattern), to which gas is conveyed by two jets in order to enlarge the flame. It is first heated until the filter is carbonised, which generally requires from ten to fifteen minutes. The asbestos cover and the platinum lid are then removed, when in general the carbonised filter begins to smoulder. The flame is then from time to time removed from under the air-bath, and the glowing ash is cautiously fanned with the lid, and finally the process of oxidation is expedited as much as possible by stirring with a long platinum rod.

An absolutely complete combustion is, however, seldom effected, but small particles of carbon remain, which is unimportant. The residue in the crucible is moistened with concentrated nitric acid, evaporated to dryness on the water-bath, the main portion of the precipitate which has been previously set aside is added, and the crucible is again heated in the air-bath, which is entirely closed. In a short time everything is completely incinerated and oxidised, so that it can be without hesitation faintly heated and fused with the open gas-flame without the slightest injury to the platinum. The ignition and weighing of the bismuth oxide thus obtained are repeated in order to be certain of the constancy of its weight.

The weighings of bismuth give in the first place values slightly too high in consequence of the traces of silica, &c., contained in commercial hydrogen peroxide. A little silica can also be introduced at times from the ammonia and from the apparatus. It is therefore advisable, previous to the commencement of the operation, to determine the quantities of silica and alumina which may be contained in a large quantity of hydrogen peroxide. For this purpose we evaporate to dryness 50 c.c. of the hydrogen peroxide in a platinum capsule with the addition of a little nitric acid. In the best samples which we obtained, we found on the average in 50 c.c. 0·005 to 0·007 grm. silica, and 0·001 to 0·002 grm. alumina and magnesia. If we wish to determine the silica by itself in the weighed bismuth oxide, we dissolve it in nitric acid, evaporate the solution in a small platinum capsule until as dry as dust, re-dissolve the nitrate anew and filter off, taking the precaution to wash the undissolved flakes of silica continuously with warm dilute nitric acid.

We have ascertained by many experiments that the silica present in the hydrogen peroxide is carried down with absolute completeness, by the precipitation of the bismuth, but is as completely re-dissolved when the recent precipitate is again taken up in hot dilute nitric acid. The filters concerned yielded on combustion only minimum traces of ash, whilst the solution of bismuth contained, in fact, the silica in question.

The ammoniacal filtrate from the precipitate of bismuth is evaporated to dryness in a deep capsule of Berlin porcelain, stirring diligently towards the conclusion, so as to leave a granular residue. It is then heated (after the removal of the stirring rod) first for some time upon an air-bath, and lastly upon an asbestos capsule until the ammoniacal salts are completely expelled. A direct heating of the porcelain capsule with a free flame is to be avoided to prevent the loss of the zinc salts; platinum capsules cannot be used for the expulsion of the zinc salts, since they are somewhat attacked, so that the precipitated zinc carbonate encloses platinum and then appears grey after ignition. The zinc nitrate remaining in the porcelain capsule is dissolved with water with the addition of a couple of drops of dilute nitric acid, freed from impurities by filtration, and the clear filtrate is precipitated as usual with sodium carbonate. The washed zinc carbonate is dried at about 100°, and the filter and the precipitate are ignited separately in a porcelain crucible. Any traces of silica, alumina, and ferric oxide may be removed by dissolving the ignited oxide in dilute acetic acid, the undissolved residue being weighed separately and deducted. Such impurities were met with only in exceptional cases. Even the purest salts of zinc may contain traces of iron.

Separation of Bismuth and Nickel.

The separation was effected exactly as directed for the separation of bismuth and zinc. In the precipitation of nickel after the previous expulsion of the free ammonia, the ammonium salts are either driven off by cautious heating, or they are disregarded, and the liquid is at once precipitated with an excess of sodium hydroxide.

Separation of Metals by Means of Ammonium Persulphate.

The authors feel themselves free to append a preliminary notice of separation of metals by precipitation as hyperhydroxide. We are not yet in a position to point out any advantage in this process.—*Berichte*, xxvii., p. 2227.

SOME RECENT CONTRIBUTIONS TO OUR KNOWLEDGE OF METALLIC REDUCING AGENTS.[*]

By H. F. KELLER.

In the extraction of metals from their oxygen compounds, carbon is certainly the most important and useful reducing agent. Its great affinity for oxygen is utilised in the manufacture of iron and steel; the commercial production of other useful metals, such as copper, lead, zinc, and tin, is accomplished, either directly or indirectly, with its aid; and under its influence even the energetic metals of the alkalis release their powerful grip upon oxygen. Contrasted with this, the use of other substances for the purpose of abstracting oxygen is almost insignificant. Is it surprising, therefore, that carbon is looked upon as the reducing agent *par excellence*, or that the very idea of reduction seems to us inseparably associated with this element?

But the reducing power of a substance depends, in a large measure, upon temperature. It is well known to chemists that, under certain conditions, many metals have affinities which are far more powerful than those of carbon. When we glance over the pages of our chemical text-books, we see described there numerous experiments based upon the superior combining power of iron, aluminium, zinc, magnesium, and the alkali metals. The great Swedish chemist who arranged the elements according to their supposed affinities in an electro chemical series, was among the first to employ the positive alkali metals for isolating and preparing other elements. His method consisted in decomposing the halogen compounds by means of potassium; and it was subsequently improved by Berzelius's distinguished disciple, Wöhler. With its aid the latter chemist not only succeeded in reducing for the first time those remarkable metals, aluminum and glucinum, but he also showed that *all* those metals, the oxides of which cannot be reduced by either carbon or hydrogen, may be obtained by the action of potassium upon their halogen compounds.

It must not be supposed, however, that the use of metals as reducing agents is confined to the laboratory and the lecture table. Practical applications of such reac-

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[*] *Journal of the Franklin Institute*, October, 1894.

tions may be less conspicuous, but they constitute, nevertheless, the basis of not a few important metallurgical processes. The "precipitation" of lead from its sulphide ores; the solution of silver by the nascent lead in the blast-furnace; the amalgamation of the same metal in the iron pan; Deville's process of extracting "silver out of clay," recently so greatly perfected by Castner and Netto—are they not essentially reductions by means of metals?

In view of the facts mentioned, it may appear strange that comparatively little progress was made for many years in the study of the reducing properties of metals. We can, however, satisfactorily account for this when we consider the great tendency of metals to form alloys; it is difficult, in many cases indeed impossible, to obtain products entirely free from the reducing metal, and it is also well known that even a trifling amount of such an impurity may seriously impair the valuable qualities of a metal. Another obstacle has been the high price of those metals, which, by reason of their more powerful affinities, could, with advantage, be substituted for carbon.

Recent improvements in the commercial production of some of these metals have partially removed the latter obstacle. Thanks to the rapid progress of electro-metallurgy, aluminum is now to be had for about half a dollar per pound; sodium, once a chemical curiosity, is manufactured on an enormous scale at a less cost even than aluminum; and magnesium, now successfully extracted from carnallite, is applied to a variety of technical uses.

The radical changes which have taken place in our views on chemical affinity, as a result of the study of thermo-chemical phenomena, and the theory that the properties of the elements are *periodic functions* of their atomic weights, have also largely contributed to awaken interest and activity in the subject of our discussion.

The remarkably high heats of formation of its oxide and chloride, as well as the great stability of these compounds, render the action of magnesium upon other oxides and chlorides particularly interesting. Clemens Winkler, of Freiberg, has presented us with a most careful and systematic investigation of the reducing action of this metal upon oxides, while Seubert and Schmidt have communicated a similar exhaustive study of its action upon chlorides.

In giving a brief résumé of the results obtained by these experimenters, I shall adhere to the order adopted by them. It is based upon the periodic system, and has the advantage of showing many interesting relations that might otherwise escape notice.

Group I.

Group I. embraces a main group consisting of lithium, sodium, potassium, rubidium, and cæsium, and a sub-group consisting of copper, silver, and gold.

Owing to the difficulty of obtaining the oxides of the alkali metals in a pure condition, the carbonates were employed. It was found that to ensure the best results three atoms of magnesium are required for every molecule of the carbonate, thus:—

$$Na_2CO_3+3Mg=3MgO+C+2Na.$$

The carbon as well as the sodium are deprived of their oxygen. It was found that, with the exception of cæsium carbonate, the alkaline carbonates *suffer reduction* to the metallic state when heated with magnesium, but that the intensity of the reaction diminishes as the atomic weight of the metal increases. Lithium, *e.g.*, whose atomic weight is only seven, was reduced with explosive violence, the metal being completely vapourised, while the tube in which the reduction was effected was shattered to pieces; potassium (atomic weight 39) and rubidium (atomic weight 85), on the other hand, were reduced quickly and without notable vapourisation.

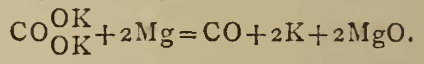
The reduction may be made in a tube of hard glass closed at one end; it is better observed, however, by conducting it in a current of hydrogen.

The preparation of potassium affords a most instructive experiment, which may well serve for lecture demonstration.

Into a wide tube of Bohemian glass a porcelain boat, containing about 2 grms. of the mixture of potassium carbonate, and magnesium is introduced. A current of perfectly dry hydrogen gas is passed through the tube, and the part of the tube surrounding the boat is gradually heated to incipient redness; the mass darkens, and upon further raising the temperature with the aid of the blast-lamp, the reduced potassium is completely expelled from the boat, exhibiting the deep green colour of its vapour, and is deposited in the form of a bright mirror in the cooler part of the tube. At the same time the hydrogen flame shows an intense violet colour. The dark residue remaining in the boat consists of magnesia and carbon. Enough potassium will have collected to show its colour, lustre; that it is sectile, fusible; its action upon water, bromine, &c.

In view of the high price of metallic potassium, the question as to whether the described reaction might not be carried out on the large scale suggested itself. Experiments showed, however, that in the absence of a gas current the distillation of the metal is very incomplete; and inasmuch as carbon monoxide forms an explosive compound with this metal, illuminating gas could not be substituted; in fact, the explosive carbonyl potassium was invariably formed when the quantity of magnesium present was insufficient for the *complete* reduction of the carbonate.

This was further proved by experiment. When two atoms only of magnesium were taken, the reaction took place according to the equation—



$$CO\begin{matrix}OK\\OK\end{matrix}+2Mg=CO+2K+2MgO.$$

More promising results were obtained by employing potassium hydroxide instead of potassium carbonate. The danger of forming the explosive body is thus avoided, while the hydrogen gas set free simultaneously with the potassium ensures the complete distillation of the latter—

$$KOH+Mg=K+H+MgO.$$

The reaction is somewhat violent, but may be moderated by adding some inert substance, such as magnesia, or by using the magnesium in the form of lumps or bars.

Winkler says, "it does not seem unlikely that the manufacture of potassium could be carried out by means of the same apparatus and the same operations which C. Netto has so successfully employed in reducing caustic soda with carbon. Into a retort filled with bars of magnesium and heated to redness, melted potash would be allowed to flow in a continuous stream, while the escaping mixture of potassium vapour and hydrogen is being cooled."

Winkler figures the cost of a pound of potassium to be about 3 75 dollars; the metal is now quoted at 28 dollars.

Beketow, who had previously made use of the action of aluminum upon potassium hydroxide, obtained only one-half of the theoretical yield owing to the simultaneous formation of potassium aluminate.

The sub-group, consisting of the heavy metals copper, silver, and gold, exhibited the reverse behaviour; the reduction was more energetic the higher the atomic weight of the metal. A very *slight* deflagration accompanied the removal of oxygen from cuprous oxide, while silver oxide was reduced with *explosive violence.* Very curiously aurous oxide was not visibly affected by the magnesium. This is explained, however, by the fact that gold oxide splits up into its constituents considerably below the ignition-point of magnesium.

Group II.

The main group comprises glucinum, magnesium, calcium, strontium, and barium; and zinc, cadmium, and mercury constitute the sub-group.

These elements are bivalent, and the action of their oxides upon magnesium is therefore—

$$R''O + Mg = MgO + R''.$$

In some cases the *hydroxides* were also used.

Glucina was easily reduced by magnesium; the mass became slightly incandescent, but some unaltered oxide was found in the residue.

There was no action observed when a mixture of magnesium and magnesia was heated in hydrogen; the oxide remained in the boat, while the metal sublimed in beautiful crystals. The existence of Beetz's sub oxide could not be confirmed.

No visible sign of chemical action occurred when lime and magnesium were heated together. The reduction proved, nevertheless, to be almost complete.

A slight incandescence attended the reduction of strontia, whilst barium oxide displayed an energetic action upon magnesium. In both cases the decomposition was apparently complete.

None of the alkaline earth metals were found to be volatile at the temperature of reduction.

The hydroxides were even more readily acted upon than the oxides; so striking and beautiful, indeed, were the phenomena observed in the cases of calcium hydroxide and strontium hydroxide that Winkler proposes to utilise them for lecture illustration and in pyrotechnics.

The reduction of the oxides belonging to the sub-group was very energetic, the resulting metals being vapourised completely. Cadmium oxide develops less energy than either zinc oxide or magnesium oxide.

Both in the main group and the sub-group, the maximum of chemical energy occurs in the second member.

(To be continued).

ON THE TECHNICAL ANALYSIS OF ASPHALTUM.*

By LAURA A. LINTON.

IN the year 1837 J. B. Boussingault published his celebrated memoir on the "Composition of Bitumens." In the researches upon which this memoir was based he had discovered that certain bitumens yielded to one class of solvents a portion of their content, and to another class of solvents another portion of their constituent hydrocarbons. He called the first portion "Petrolene" and the second portion "Asphaltene" (*Annales de Chemie et de Physique*, lxiv., 191).

In 1827 (*Bull. Soc. Chim.*, xvii., 156) Le Bel and Muntz went over the same ground, and in 1883 Le Bel again went over it, adding a few facts in relation to other bitumens than those previously examined, but leaving the two substances, petrolene and asphaltene, practically where he found them (*Bull. Soc. Chim.*, l., 359).

In 1837 the conclusions based on chemical research were far less exact than at the present time, and Boussingault concluded that the substances, petrolene and asphaltene, were simple substances, and also that they were identical from whatever sources they were derived. In this conclusion Le Bel, in a measure, appears to coincide.

It, however, requires no argument to prove, to any one at all familiar with the subject, that petrolene is nothing but a name that covers a great variety of substances, radically unlike, that exist in different forms of bitumen and are only related, in this instance, as being held in solution by a certain limited number of menstrua, and which include the whole list of paraffines and iso-paraffines, the olefines, the benzenes, and additive benzenes, with many other less abundant and well-known substances.

Ethyl ether and so-called petroleum naphtha, which latter is an indefinite mixture of fluid paraffines and iso-paraffines of high specific gravity, are the solvents used; but no determination has been made as to the influence of proportion in the mixtures of the substances dissolved, or as to the relative solvent powers of the two menstrua upon the different constituents of these mixtures. In fact, petrolene is nothing but a name which at present covers a vast expanse of the unknown.

It can be safely said that probability favours the assumption that asphaltene is a little more definite; but no certainty attaches to the identity of asphaltene from different sources or of asphaltene dissolved by different menstrua.

Therefore, in a general way, it may be said that asphaltene is that portion of the different forms of bitumen that is soluble in carbon disulphide, chloroform, benzene, and a few other less well-known liquids, and is not soluble in the menstrua that dissolve petrolene.

As the bitumens examined by the French chemists above mentioned have never assumed commercial importance, the questions relating to petrolene and asphaltene have remained matters of scientific interest only. However, since asphalt paving has become a business involving the expenditure of large sums of money, these problems are beginning to assume a wide importance outside the laboratory of the chemist, and to demand from technologists very serious consideration. Within recent years large numbers of so-called analyses have been reported, which represent various attempts to determine and set forth the relative value of many samples and kinds of asphaltum that may or may not be suitable for the many uses to which asphaltum is applied, but more particularly with reference to street paving. Prominent among the chemists who have been more or less extensively engaged in these analyses of alphaltes, are Mr. Clifford Richardson, Dr. Henry Leffmann, Dr. Samuel P. Sadtler, and Dr. De Smedt.

A perusal of the numerous published reports of Mr. Richardson reveals the fact that in his tests the solvents used for the extraction of petrolene and asphaltene were petroleum ether and carbon disulphide, while Drs. Leffmann and Sadtler, in their investigations and tests of asphaltes, used alcohol—presumably ethyl-alcohol,—carbon disulphide, and ether, as shown by the report submitted to the Citizens' Municipal Association and the Trades League of Philadelphia.

Neither of these gentlemen describe any process or method employed in obtaining the results stated. It is hardly consistent with the nature of the reports that they should. Nor has Mr. Richardson, in an article published in the *Journal of Analytical and Applied Chemistry*, in the numbers for December, 1892, and January, 1893, given any detailed description of the process he employed in order to obtain the numerous results of analyses that he there uses.

But little satisfaction can be derived from consulting Allen's encyclopædic work, so exhaustive upon every subject relating to technical organic analysis ("Commercial Organic Analysis," by Alfred H. Allen, London, 1886, ii., 375, 376, 377).

We find therein the following statements and notes concerning the solvents and methods used in the analysis of asphaltes:—"For the determination of the *total bituminous matters* in asphalte rock and mixtures containing it, C. T. Kingzett extracts the air-dried sample with freshly distilled Russian oil of turpentine, evaporates (*Analyst*, viii., 4) the resultant solution, and weighs the residue. The matter insoluble in turpentine is washed with ether, the *calcium* and *magnesium* carbonates dissolved in hydrochloric acid, and the washed insoluble *siliceous matter* weighed."

"H. P. Cooper prefers carbon disulphide for dissolving out the bituminous matters from asphaltic mixtures."

Allen adds in a note, "The carbon disulphide employed for dissolving the bituminous matter must not contain free sulphur. It may be replaced by chloroform or

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* *Journal of the American Chemical Society*, xvi., No. 12.

benzene (coal tar naphtha). If the residue left after extraction be dark coloured, foreign organic matters of valueless nature are present. Their proportion may be determined by igniting the weighed residue left after dissolving out the asphaltum, re-carbonating it with ammonium carbonate, again gently heating it and re-weighing. The loss of weight is the amount of *non-bituminous* organic matter present. In the case of samples leaving a white residue after exhaustion with carbon disulphide, the bituminous matter may be simply and accurately ascertained from the loss on ignition, taking care to re carbonate the lime before weighing."

In another note, page 377, he says: "Five grms. of the finely divided sample were digested for one hour with 50 c.c. of petroleum spirit (sp. gr. 0·7), and the mixture frequently agitated. The liquid is then boiled for a short time, decanted, and the residue boiled with another quantity of 25 c.c. of petroleum spirit. This treatment is repeated eight or ten times until the exhaustion is complete."

"E. Davies (*Pharm. Journ.*, [3], xiv., 394) reports that none of the organic matter in Val de Travers asphalte is insoluble in petroleum spirit."

Now, when we take into consideration the fact that turpentine, carbon disulphide, ether, chloroform, and benzene have been used indiscriminately by chemists in the extraction of asphaltene, the question very naturally arises, are the results that have been and that are being obtained by these different methods of analysis strictly comparable—that is, are they convertible terms? Will the same asphalte treated with different solvents show in each case the same percentage composition? If not, then it is evident that asphalte taken from different localities and subjected to dissimilar methods of analysis, cannot yield results of any value so far as purposes of comparison are concerned. Then again, if turpentine, carbon disulphide, and chloroform give a different proportion of asphaltene in the same asphalte, it is just as evident that asphaltene, instead of being a definite chemical substance, is a mixture, which mixture would doubtless vary in different asphaltes.

It was for the purpose of determining whether petroleum ether (paraffines), California naphtha, and ethyl ether are interchangeable solvents of petrolene, and whether turpentine, carbon disulphide, and chloroform are interchangeable solvents of asphaltene, that the research, the results of which are here given, was undertaken. That a series of such tests, faithfully carried out, should lead to the establishment of a method of analysis applicable to all asphaltes, and, at the same time, reveal something regarding the real nature of petrolene and asphaltene, was inevitable.

The specimens analysed were furnished me by Prof. S. F. Peckham, chemist of the Union Oil Company of California, and were as follows:—

1. *Crude Trinidad Asphaltum.*—From the Warren-Scharf Asphalte Company, of New York City. This specimen contained little or no water, as for several months it had been broken in small pieces, and so had lost the water which this asphaltum generally contains.

2. *Cuban Asphalte.*—A commercial sample obtained in New York City.

3. *Kuban Residuum.*—An artificial asphalte obtained from the distillation of Kuban petroleum from the western extremity of the Caucasus Mountains, Russia.

4. *Egyptian Asphalte.*—An Assyrian asphalte taken from the Dead Sea and imported into Egypt. This specimen was obtained in New York City.

5. *Asphaltic Rock.*—From Val de Travers, Switzerland. This asphalte was a sample of natural rock obtained at the office of Wm. H. Delano, representative of the French Company in New York City.

6. *Seyssel Asphaltic Rock.* — From the well-known locality in eastern France, obtained from the same source as No. 5.

7. *Turrellite.*—From a deposit lately discovered in Uvalde County, Texas, consisting of a mass of sea-shells cemented together by bitumen into a solid rock mass. It occurs in a rock formation said to be of Jurassic age, in which formation the Val de Travers rock also occurs. This specimen was obtained from the office of the Litho-carbon Company of New York City.

8. *Kentucky Asphaltic Rock.*—Obtained from Marshall Morris, Esq., Louisville, Ky.

9. *An Asphaltic Mineral.*—Resembling Gilsonite; reported as coming from Utah.

10. *California Maltha.*—Taken from a well at Summerland, on the coast, near Santa Barbara.

11. *Asphaltum.*—From mines recently opened near Asphalto, Kern County, California, in the eastern foot hills of the Coast Range Mountains, about 30 miles west of Bakersfield.

12. *Asphaltic Sandstone.*—From San Luis Obispo, California.

13. *Asphaltum.*—Picked up on the beach at San Buena Ventura, California, washed in from the Santa Barbara channel.

14. *Asphaltum.* — From the Ojai ranch, Ventura County, California.

15. *Grahamite.*—A so-called asphaltum taken from a vein in Ritchie County, West Virginia.

16. A portion of a compressed brick made from the asphaltic rock taken from the Seyssel mines. Exhibited at the Columbian Exposition.

17. *Hard Artificial Asphalte.*—An asphaltic residue obtained from the distillation of petroleum obtained near Santa Paula, California. It is known in the refinery of the Union Oil Company, of California, as grade "B."

18. *Soft Artificial Asphalte.*—From the refinery of the Union Oil Company, of California, at Santa Paula. Grade "D."

19. *Asphaltic Pavement.* — Obtained from Franklin Avenue, Buffalo, N.Y. It was laid in 1878, of Trinidad asphalte, wax tailings, and very fine sand. It is remarkable as having been laid for 15 years with almost no need of repairs.

20. *Asphaltic Pavement.* — From Governor's Island, New York Harbour, laid within the Fort at an unknown date, but so old that it has begun to break up from natural causes. Obtained from J. A. W. Pine, of New York City.

21. *Dubb's Artificial Asphalte.*—A so-called asphaltum obtained in operating the Dubb's patent process for the manufacture of asphaltum by adding sulphur to hot Lima-tar, and thereby burning out the hydrogen. This is an asphalte only in name. The specimen was obtained from J. A. W. Pine, of New York City.

22. *Roofing Pitch.*—Obtained from the Mica Asphalte Company, of New York City.

23. *Pitch.*—Obtained as a residuum in the distillation of Scotch blast-furnace tar. This specimen was obtained from the same source as Nos. 20 and 21.

In making tests to determine the best method to be used in the analysis of asphaltes, the well-known Trinidad and Cuban asphaltes were used, and all analyses were made in duplicate. In the case of asphaltes rich in bituminous matter, about a half grm. of the material, finely powdered, was used, but in the case of asphaltes in which the mineral matter constituted a large proportion, the quantity was increased to several grms.

The sample was weighed in an Erlenmeyer flask and digested over night in about 50 c.c. of petroleum ether; in the morning the clear solution containing the dissolved petrolene was passed through a balanced filter, and a fresh portion of petroleum ether added to the contents of the flask. The second digestion was continued for two or three hours, when the solution, as before, was filtered off, and the process repeated until the whole of the petrolene had been removed. The contents of the flask were then thrown upon the filter and thoroughly washed with petroleum ether. Cold turpentine was then poured upon the filter in successive portions until the filtrate passed through colourless, when the assumption was made that all the asphaltene and consequently all the bituminous matter had been removed.

The remaining organic matter, not bituminous, was determined by difference, that is, the residue on the filter, after digestion in turpentine, was washed with ethyl alcohol, dried, and weighed, in order to determine the percentage of asphaltene, after which the residue was burned in a platinum crucible, the difference in weight representing the organic matter not bituminous.

The contents of the crucible were now purely inorganic, and, in the case of most alphaltes, the residuum was sand more or less coloured with iron.

The analysis of Trinidad asphalte under this treatment gave so low a percentage of asphaltene, and so large a proportion of organic matter not bitumen, that it was clearly evident that *cold* turpentine had not dissolved, and could not dissolve, all of the asphaltene.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, December 14th, 1894.

Prof. W. E. Ayrton and Mr. H. C. Haycraft communicated a paper on a "*Students' Simple Apparatus for Determining the Mechanical Equivalent of Heat.*"

Mr. Haycraft, who read the paper, explained that the object at which the authors had aimed was the construction of an apparatus which could be placed in the hands of junior students, and by means of which a result correct within one per cent could be obtained without the introduction of troublesome corrections. The method employed is the electrical one, und the measurements to be made are (*a*) the value of the constant current passed through the resistance, as given by a direct reading am-meter; (*b*) the average value of the P.D. between the terminals of the resistance, as given by a direct-reading volt-meter; (*c*) the mass of water heated *plus* the water-equivalent of the containing vessel, resistance coil, and stirrer; (*d*) the rise of temperature of the water; (*e*) the time during which the current is passed. Of these the measurements (*a*), (*b*), (*c*) can be effected without the introduction of an error anything like as great as one per cent. The case of (*d*) and (*e*) is different. The rise of temperature, to be measured with accuracy, should be fairly considerable, and the same remark applies to the time of heating as measured by an ordinary stop-watch. At the same time, if these two quantities are made unduly great, there will be too great a ratio of heat lost to heat generated during the experiment. The authors consider that, with a given amount of electrical power available, the best conditions will be obtained by making the percentage accuracy of the temperature measurement, the percentage accuracy of the time measurement, and the percentage of generated heat lost by surface cooling, equal. Hence they determine the mass of water to be used, and the time of heating which may be expected to give the best results. The immersed conductor is a strip of manganin about 0·25 inch wide, 0·03 inch thick, and 5 feet long, which is bent into a series of zigzags so as to form a kind of circular gridiron, the successive portions of strip lying all in one plane, aad the whole being held rigid by a strip of vulcanised fibre, to which each portion of the strip is screwed. Another precisely similar grid is placed 3 inches below the first, and the two are joined in series, and are mechanically connected together by thin vulcanite pillars. The water is contained in a glass beaker of just sufficient diameter to take the framework of manganin strip. This latter exposes a considerable surface (about 400 sq. c.m.) to the water, and is moved bodily up and down during the experiment, thus constituting an efficient stirrer. To allow sufficient freedom of movement, electrical connection is made by means of very flexible leads, each made up of about 210 thin copper wires. The results obtained by students for the heat-equivalent of the watt-second have an average deviation from the mean, if several experiments are made, of less than one-half per cent; and they agree with the best standard determinations within one per cent.

Mr. Griffiths thought it unadvisable to provide junior students with apparatus from which every source of error had been eliminated; they were thus led to underrate the difficulty of an experiment, and the care required to obtain reasonable accuracy.

Prof. Carey Foster agreed generally with Mr. Griffiths, and deprecated the use of direct-reading am-meters and volt-meters in experiments of this kind. He thought it preferable that a student should learn to reduce instrumental readings to absolute measure for himself.

Prof. S. P. Thompson dissented from the opinions expressed by the two previous speakers, and thought it was an advantage to students to have the use of direct-reading instruments.

Dr. Sumpner described a simple method which he had employed for measuring the mechanical equivalent of heat, and which depended on the heating of a stream of water as it flowed through a pipe containing the current conductor.

Prof. Rücker was inclined to take an intermediate view of the questions that had been raised. He thought that students should take for granted as little as possible concerning their instruments, but to verify every point, even if practicable, would occupy much time that might be otherwise more profitably employed.

Prof. Ayrton replied, and explained that the calibration of am-meters and volt-meters would be part of the work of a student at another part of his course.

A paper by Prof. Ayrton and Mr. E. A. Medley entitled "*Tests of Glow-lamps and Description of the Measuring Instruments Employed*," was commenced by Mr. Medley, the latter part of the paper being held over till next meeting.

The object of the investigation was to find at what E.M.F. glow-lamps could be most economically run. Too low an E.M.F. gives a low efficiency, and too high an E.M.F. renders the lamps short-lived, so that there must be (for a given lamp) a certain E.M.F. which is more economical to work at than any other. It was also pointed out that, as glow-lamps deteriorate and become less efficient with use, it may be an economy to discard a lamp before the filament actually breaks. The lamp is then said to have reached the "smashing-point." Accumulators were used to drive the lamps, automatic apparatus being used to keep the E.M.F. constant, and when a lamp-filament broke, the fact was automatically recorded on a tell-tale.

NOTICES OF BOOKS.

Organic Chemistry. Part II. By W. H. Perkin, jun., Ph.D., F.R.S., Professor of Organic Chemistry in the Owens College, and F. Stanley Kipping, Ph.D., D.Sc., Lecturer and Assistant in the Chemical Research Laboratory. Central Technical College, City and Guilds of London Institute. London and Edinburgh: W. and R. Chambers, Limited, 1895. Small 8vo., pp. 552.

This work, along with Part I., which appeared previously, forms a very good introduction to the study of organic chemistry as at present understood. The present volume is mainly devoted to the aromatic compounds, but some of the concluding chapters are taken up with an account of the alkaloids and of dyes and their applications, and lastly of stereo-isomerism.

The concluding paragraph of this work refers to the use of a minute organism, *Penicillium glaucum*, in effecting organic separations. Perhaps this is the first dawn of a series of novel methods.

Indigo is here mentioned as a natural dye, the various syntheses by which it has been artificially produced, though of very great theoretical interest, being too expensive for practical purposes.

It is here mentioned that the sodium salt of indigodisulphonic acid, extensively used in dyeing, is known as "indigo carmine." This is certainly the case on the Continent, but British dyers cannot fortunately see the sense of giving the name of carmine to a blue colour.

This book will be an excellent guide for students intending to devote themselves to tinctorial chemistry. It may be advantageously used before entering upon works of a more special character.

Drs. Perkin and Kipping have presented the English-speaking chemical public with one of the best text-books of its class.

Elementary Qualitative Chemical Analysis: Adapted for Use in the Laboratories of Colleges and Schools. By Frank Clowes, D.Sc., and J. B. Coleman, F.I.C. London: J. and A. Churchill, 1894. Post 8vo., pp. 180.

This work is especially adapted for junior students and technical students rather than for such as take up chemistry from a professional point of view. We may, however, remark that the requirements of the technical chemist are in this country fixed at too low a standard. The less common metals are not taken into consideration, and the authors give no directions for the recognition of organic bodies. Blowpipe chemistry is not overlooked, but spectroscopic reactions are not mentioned.

The instructions given are clear, intelligible, and in accordance with our present state of chemical knowledge. For those whose time will not allow them to take a more thorough course, this work may be recommended.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 24, December 10, 1894.

At the meeting of the Academy the Perpetual Secretary made the official announcement of the death of Ferdinand de Lesseps, which took place at Chesnaye, in Indre, on December 7. The deceased had reached the age of 89 years.

Varieties of Graphite.—Henri Moissan.—Whatever variety of carbon may be taken for experiment, a sufficient rise of temperature always converts it into the state of graphite. This graphite may be either amorphous or crystalline; its density varies from 2·10 to 2·25. Its temperature of combustion in oxygen borders on 660°. There are several varieties of graphite, just as there exist several varieties of amorphous carbon and of diamond. The stability of graphite increases with the temperature to which it has been heated. This fact is shown by the greater or less resistance which graphite presents to conversion into graphitic oxide. In proportion as the melting-point of the metal increases, in which the graphite is produced, its difficulty of oxidation increases. It is thus that by a rise of temperature we may transform a graphite, easily attackable, like that of Ceylon, into a graphite much more resistant.

Phosphate from the "Grand Connetable."—A. Audouard.—The islet of Grand Connetable, situate at 27 miles to the east of Cayenne, possesses a very important deposit of aluminium phosphate. It is light, amorphous, and has been hitherto used only for the manufacture of alum. Its percentage composition is—

Phosphoric acid	39·10
Silicic ,,	1·70
Sulphuric ,,	0·06
Carbonic ,,	traces
Chlorine	traces
Alumina	25·59
Ferric oxide	8·03
Lime	1·40
Magnesia	traces
Water expelled at 105°	21·24
Water at redness	2·50
Not determined	0·38
	100·00

Its desiccation must be effected a little below 100°. It gives off nothing to cold water, but it is very soluble in acids and in ammonium citrate, and is hence readily assimilable.

On Pectose and on the Pectic Fermentation.—G. Bertrand and A. Mallèvre.—Pectase, though a ferment, is not alone able to coagulate pectine. It induces this transformation only in presence of a soluble salt of calcium, strontium, or barium. The precipitate formed under these conditions is not, as hitherto supposed, pectic acid, but an alkaline earthy pectate.

A New Procedure for Purifying Alcohols, Sugars, and other Organic Products.—E. Maumené.—This new procedure is the addition of potassium permanganate.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., Nos. 16 and 17.

This number contains an account of the life and researches of the late Jean Charles Galissard de Marignac, including a valuable list of his memoirs in the *Comptes Rendus*, in *Liebig's Annalen*, the *Journal fur Praktische Chemie*, the *Ann. der Chemie et Pharmacie*, the Chemical News, the *Phil. Mag.*, &c. Not a few of these papers are devoted to the rare earths and to the determination of atomic weights. This compilation is due to the persevering industry of M. E. Ador.

Study of certain Novel Phenomena of Fusion and Volatilisation produced by means of the Heat of the Electric Arc.—Henri Moissan.—Already inserted.

Chemical Classifications and Symbols in Antiquity and in the Middle Ages.—M. Berthelot.—The metals and their derivatives formed the basis of the earliest chemical classification. In contradistinction to them were two groups of substances, *spirits*, or volatile bodies, and *stones*, regarded as fixed and infusible. The discovery of sulphuric and nitric acids has been erroneously ascribed to the Arabs. According to authentic texts they were isolated and distinguished only after the 13th century, and their exact knowledge was only developed by degrees in the course of the 16th century. From this memoir it appears that chemistry took its rise, not in alchemy, but in technology.

Preparation of a "Sprouting" Variety of Graphite.—Henri Moissan.—The author has succeeded in preparing a variety of sprouting graphite analogous to that which occurs in nature. His methods are either the sudden cooling of cast-iron or the solution of carbon in platinum at high temperatures. The cause of the sprouting is a sudden liberation of gases.

New Experiments on the Reproduction of the Diamond.—Henri Moissan.—The author obtains a variety of carbon black or transparent. Some specimens have a distinct crystalline appearance, a specific gravity of from 3 to 3·5; they scratch ruby and resist twelve successive treatments with a mixture of dry potassium chlorate and fuming nitric acid. They burn in oxygen at a temperature of 900°, yielding about four times their weight of carbon dioxide. These properties are possessed solely by the diamond.

Some Observations on the Amidochromates.—G. Wyrouboff.—The author shows that the alleged amidochromates have no existence any more than the nitrochromates. He cautions young chemists not to rely on the purity of commercial products, but always to purify them before use.

Remarks on certain Hydrated Metallic Chlorides, with reference to a Paper by P. Sabatier.—H. Lescœur.—The writer's researches and those of Sabatier, though concerned with the same substances, are distinct. Sabatier has measured the calories of dissociation, and the author the tensions.

Preparation in the Electric Furnace of some Refractory Metals: Tungsten, Molybdenum, and Vanadium.—Henri Moissan.—Already inserted.

Certain Articles of Copper of very Ancient Date obtained from Chaldea.—M. Berthelot.—The objects found consist mainly of 77·7 per cent of copper, and are entirely free from tin, zinc, lead, iron, and silver. Hence they prove the existence of an age of copper preceding the age of bronze. They must have been made at an age anterior to 2000 B.C. At that date bronze and tin do not appear to have been wrought either in Chaldæa or in Egypt.

Certain Novel Objects of Copper from Ancient Egypt.—M. Berthelot.—The term bronze was used at one time by antiquarians and historians in a vague manner so as to include copper, brass, and bronze. In a similar manner *nitre*—a salt unknown in antiquity—has been used for *natron* and sodium sulphate or carbonate; sal-ammoniac was the name of a fixed salt, and *azur* served for cinnabar or vermilion.

Volatilisation of Silica and Zirconia, and on the Reduction of these Substances by Coke.—Henri Moissan.—Zirconia and silica melt rapidly in the electric furnace, and if the experiment is prolonged for seven or eight minutes, they boil and assume the gaseous condition.

Researches on the Iron of Ovifak.—Henri Moissan.—In certain specimens of the iron of Ovifak entrusted to us by Daubiée we have recognised distinctly in one sapphire, in three amorphous carbon, in two sprouting graphite, in one normal graphite, but in none of them diamonds, whether black or transparent.

Nitromethane and its Homologues.—MM. Berthelot and Matignon.—The nitro-derivatives of the formenic carbides are formed, setting out from nitric acid with liberation of heat comparable to that from nitrobenzene and its analogues. The greatness of this liberation explains the stability of these compounds and the fundamental difference of their reactions from those of the nitric ethers.

Propylene and Trimethylene Sulphates.—M. Berthelot.—A thermo-chemical paper not admitting of useful abstraction.

Reaction of the Alcohol Acids.—A. Berg.—Uffelmann has recently indicated for lactic acid a reagent obtained from a very dilute solution of ferric chloride so as to obtain a slight amethyst colour. This solution changes to a brilliant yellow under the influence of lactic acid. The author finds that this reaction is generally applicable to the acids possessing an alcoholic function, and that the phenol added to the ferric salt takes no part in the reaction. The reagent is best obtained by adding to 100 c.c. of distilled water two drops of ferric chloride at 45° B. and two drops of hydrochloric acid at 22° B. This reagent produces an intense yellow with the glycolic, lactic, α-oxyisobutyric, glyceric, gluconic, malic, tartaric, citric, mucic, and phenylglycolic acids.

Methyl and Ethyl Nitrosobutyrates.—G. Lepercq.—Not suitable for abstraction.

Action of Alkaline Nitrites upon α-Ethyl Bromopropionate.—G. Lepercq.—If we heat in the water-bath by cohobation the ethyl bromopropionate with its own weight of absolute alcohol and sodium nitrite, torrents of gas are evolved. If the liquid is poured into water, there is precipitated a reddish oil. This oil on purification becomes yellowish, and has the composition $C_{10}H_{16}N_2O_7$.

Action of Bromine upon the Oxide Ethers in Presence of Sulphur.—M. Genvresse.—The products of this reaction are alcoholic bromides and bromated aldehyds.

Various Notes.—E. Nægeli.—These notes treat of benzoyl anilide, of benzoyl chloride and aniline, of the behaviour of benzoic acid and aniline, of benzenylamidothiophenyl, of mononitrobenzenylamidothiophenyl, and of benzeneazophenol ethylate.

Researches on Phenylhydrazine. Action of Oxygen and of Water. Formation of Salts.—M. Berthelot.—A thermo-chemical paper not sufficiently important for insertion in full.

Action of Sulphuric Acid upon Camphene.—G. Bouchardat and J. Lafont.—The products of this reaction are the ether of the borneol of inactive camphene, the principal product; the sulphuric borneol acid yielding on further saponification borneol of inactive camphene and a small quantity of the polymers of camphene, the most abundant of which is $C_{40}H_{32}$.

A New Acid Isomeric with Campholic Acid.—M. Guerbat.—The composition of this acid is $C_{10}H_{18}O_2$. Its vapour density is 4·90, or by calculation 5·83. The acid is a colourless oily liquid which does not solidify at −20°. Its odour resembles that of valerianic acid. It boils at 180°—181°. At 0° its specific gravity is 0·9941; its rotatory power is $\alpha_D = + 24° 38'$. It is almost insoluble in water, but miscible with alcohol and ether. It does not fix bromine. Unlike campholic acid, it behaves with coloured reagents like a strong acid. It is not precipitated from its alkaline solutions by carbonic acid. It is etherified at the ordinary temperature by the action of alcohol and hydrochloric acid, and the ether is saponifiable.

MEETINGS FOR THE WEEK.

Monday, 7th.—Royal, 4.30.
—— Society of Chemical Industry, 8. (At Burlington House). "An Investigation of the Natural Solidified Sodium Sulphate Lakes of Wyoming, U.S.A." by Dr. D. Harvey Attfield, M.A.
Tuesday, 8th.—Royal Institution, 3. "The Working of an Electrical Current," by Prof. J. A. Fleming, F.R.S.
—— Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers, 8.
—— Photographic, 8.
Wednesday, 9th.—Geological, 8.
Thursday, 10th.—Institute of Electrical Engineers, 8.
—— Mathematical, 8.
Friday, 11th.—Physical 5. "On the Passage of an Oscillator Wave-Train through a Plate of Conducting Dielectric," by G. U. Yule. "On the Heat of Vapourisation of certain Organic Liquids," by Prof. Ramsay, F.R.S., and Miss Dorothy Marshall, B.Sc. "The Thermal Conductivity and Emissivity of Brass in Absolute Measure, and the Influence of Curvature on Emissivity," by N. Eumorfopoulos, B.Sc. "Observations on Emissivity and Curvature," by A. W. Porter, B.Sc. "Experiments on the Production of Combination Tones," by Dr. C. V. Burton.
—— Astronomical, 8.

TO CORRESPONDENTS.

Potassium Cyanide.—A correspondent wishes to know the names of manufacturers of cyanide of potassium 98/100 per cent.

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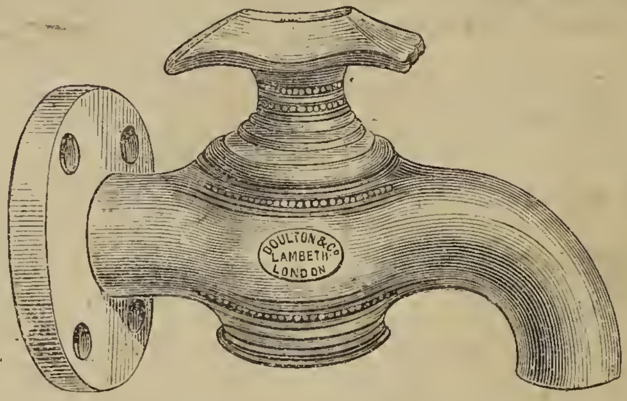

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January 4, 1895.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1833.

SULPHATE OF IRON AS A MANURE FOR POTATOES.

By E. WIGHTMAN BELL, F.C.S.

The use of sulphate of iron as a manure for certain crops has been advocated by several chemists, more especially by Dr. A. B. Griffiths, who has published many very satisfactory results from its use, particularly in the case of beans, turnips, potatoes, and clover. This opinion has, as a rule, been confirmed. Still, it was thought that further experiment on the subject might be useful.

The tables given below show the result of the addition of iron sulphate to other manures commonly used with potatoes. Each plot measured $\frac{1}{30}$th of an acre, and, as far as possible, under similar conditions as to weather, aspect, and composition of the soil (*i.e.*, all were in the same field). My thanks are due to Mr. T. Clayton, Spalding Marsh, for kindly allowing me to make the experiments on his land.

The soil is a rather heavy silt, and contains 4·54 per cent organic matter, 0·20 per cent phosphoric acid, and 4·22 per cent ferric oxide (only a very small quantity of which, however, is in a readily soluble condition).

The previous cropping was two years clover, the first crop being mown and the second eaten off by sheep each year. The clover was sown with wheat, which succeeded oats after mangolds. The whole of the plots were planted on the same day (April 4), and in very dry weather, and each received the same quantity of potatoes, which were "The Bruce."

Table I.—*Phosphates With and Without Iron Sulphate.*

No.	Manure per acre.	Yield per acre.
1.	3 cwt. mineral superphosphate	9 tons 11 cwt.
2.	The same, with ½ cwt. iron sulphate	11 tons 0 cwt.

The above shows an increase at the rate of 1 ton 9 cwt. per acre from the use of the iron salt.

Table II.—*Phosphates and Sulphate of Ammonia With and Without Iron.*

No.	Manure per acre.	Yield per acre.
3.	3 cwt. mineral superphosphate and 1 cwt. ammonium sulphate	10 tons 12 cwt.
4.	The same, with ½ cwt. iron sulphate	11 tons 7 cwt.

Showing an increase at the rate of 15 cwts. per acre on the plot manured with iron, which more than fifteen times repays the outlay on the iron salt.

According to analyses by Dr. Griffiths of the ashes of potatoes grown with and without sulphate of iron it would appear that iron has the power of replacing potash in plants so treated. The composition of the ash of the crops of potatoes was not ascertained, but it was found that kainit and superphosphate did not give as large a yield of tubers as super. and iron sulphate.

Plot 5. { 3 cwt. mineral superphosphate and 1 cwt. kainit.. . .. .. } Yielded 8 tons 16 cwt.

In this case the addition of kainit has decreased the yield by super. only, by 15 cwts. (*vide* Plot 1), and is 2 tons 4 cwts. less than Plot 2. The reason for this diminished yield is not yet ascertained, but may probably be due to excess of saline matter, as it was found that the addition of either ammonium sulphate or iron sulphate further lowered the yield.

From the above results it seems that ferrous sulphate has a decidedly beneficial action on potatoes when used in conjunction with phosphates and ammonia.

NOTE ON THE

COMPARATIVE ANTISEPTIC ACTION OF THE PHENYL-SUBSTITUTED FATTY ACIDS.

By J. PARRY LAWS, F.I.C.

In the Thirteenth and Fourteenth "Annual Report of the Medical Officer to the Local Government Board," it has been shown by Dr. Klein and myself in experiments with phenol, phenolacetic acid, and phenolpropionic acid that the last-named had a more powerful antiseptic action on a pure culture of anthrax bacilli free from spores than phenylacetic acid, and that these acids were in turn much more powerful than phenol. I therefore thought that it would be interesting to ascertain whether the next higher member of this series of fatty acids, viz., phenylbutyric acid, possessed a more powerful action than phenylpropionic acid. In order to prepare phenylbutyric acid, I adopted, with slight modification, the process described by Fittig and Jayne (*Annalen Chem. Phys.*, ccxvi., p. 97). Instead of reducing the isophenylcrotonic acid with sodium amalgam, and carefully neutralising the alkali set free, it was reduced by heating with hydriodic acid (sp. gr. 1·7) and red phosphorus in a flask to which an inverted condenser was attached. Water was then added to the flask, and the contents filtered. The solid residue was dissolved in ammonia to separate the phosphorus, the acid re-precipitated from solution, and extracted with ether. The ethereal solution was dried, and the ether evaporated off. The acid distils about 280° C., and solidifies to a crystalline mass. When purified by crystallisation from water it softens at 48° C. and melts at 51° C. On analysis the following results were obtained:—

	Found.	Calculated for $C_{10}H_{12}O_2$.
Carbon	72·88	73·17
Hydrogen . ..	7·12	7·31

By using the above modification of Fittig and Jayne's process, a relatively much larger yield of the phenylbutyric acid is obtained. I take this opportunity of expressing my indebtedness to Mr. J. E. Marsh, M.A., for the valuable help that he gave me in the preparation of this acid in the chemical laboratory at Oxford.

There are two modes of action by which the influence of any given agent on the life and growth of a specific infective or septic micro-organism may be judged.

1. The restraining influence. 2. The killing power. The restraining influence of any substance is found by determining the smallest percentage of the agent which it is necessary to add to a favourable soil in order to prevent the development of the organism under observation. The killing power is found by determining the amount of substance it is necessary to dissolve in a liquid medium favourable to the growth of the organism, so that when the organism is sown in this mixture and transferred after a given time to a virgin soil its vitality may be so impaired that it is incapable of any development.

The following are the details of the experiments made to determine the restraining influence and killing power of phenylbutyric acid on sporeless anthrax bacilli. The cultivating medium being peptone broth and the temperature of incubation 35° C.

Restraining Influence.

Expt. I.—Solution containing 1 part of acid in 1000 of broth.

0·100 grm. in 100 c.c.

Five tubes inoculated with anthrax were sterile after six days.

Expt. II.—Solution containing 1 part of acid in 2000 of broth.

0·050 grm. in 100 c.c.

Five tubes inoculated with anthrax were sterile after six days.

Expt. III.—Solution containing 1 part of acid in 4000 of broth.

0·025 grm. in 100 c.c.

Five tubes inoculated with anthrax. After twenty-four hours two of the five tubes showed fair growth, the three remaining tubes showed copious growth after forty-eight hours.

Expt. IV.—Solution containing 1 part of acid in 3500 of broth.

0·0286 grm. in 100 c.c.

Five tubes inoculated with anthrax. All showed copious growth on second day; growth somewhat restrained for the first twenty-four hours.

Expt. V.—Solution containing 1 part of acid in 3000 of broth.

0·033 grm. in 100 c.c.

Five tubes inoculated with anthrax showed fair growth on second day.

Expt. VI.—Solution containing 1 part of acid in 2500 of broth.

0·040 grm. in 100 c.c.

Five tubes inoculated with anthrax. All five tubes sterile after five days' incubation.

Expt. VII.—Repetition of Experiment VI.

Five tubes inoculated with anthrax remained sterile after five days' incubation.

Killing Power.

In determining the filling power $\frac{1}{10}$ of a c.c. of a sporeless anthrax culture was mixed with 10 c.c. of peptone broth solution containing a known quantity of phenylbutyric acid. At intervals of five, ten, fifteen, twenty, and thirty minutes, minute quantities were transferred from this mixture to a suitable soil, to determine what effect the exposure to the antiseptic had produced upon the life of the organism.

Expt. I.—Solution containing 1 part of acid in 1000 of broth.

0·100 grm. in 100 c.c.

All the tubes inoculated at the above intervals with the exception of the thirty min. tube were fertile.

Expt. II.—Solution containing 1 part of acid in 500 of broth.

0·200 grm. in 100 c.c.

Five minutes' exposure to this strength was sufficient to kill the bacilli.

Expt. III.—Solution containing 1 part of acid in 650 of broth.

0·153 grm. in 100 c.c.

Only the tube inoculated after five minutes' exposure fertile, the remainder showed no sign of growth after prolonged incubation.

Expt. IV.—Solution containing 1 part of acid in 700 of broth.

0·143 grm. in 100 c.c.

Only the five minutes' tube fertile. The remaining tubes sterile after long incubation.

It will be seen from the above experiments that phenylbutyric acid restrains the growth of anthrax bacilli, when present in the proportion of 1—2500, and that it kills the *sporeless* bacilli when they are exposed for thirty minutes to a solution of 1 in 1000, or for ten minutes to a solution of 1 in 700.

In the following table I have compared the relative restraining and killing powers of phenol, phenylacetic, phenylpropionic, and phenylbutyric acids on anthrax bacilli:—

	Phenol.	Phenylacetic acid.	Phenylpropionic acid.	Phenylbutyric acid.
Restraining power ..	1—700	Not determined.	1—1900	1—2500
Killing power	1—200	1—450	1—600	1—1000
Length of exposure	45 mins.	30 mins.	30 mins.	30 mins.

It is interesting to note that the phenyl-substituted fatty acids increase in antiseptic power with the increase in the molecular weight of the acid, whereas Duggan (*American Chem. Journal*, vii., 62) has shown that in the fatty acids series itself the converse holds good, formic acid being more powerful than propionic acid in restraining the growth of *Bacillus subtilis.* His results are as follows:—

Formic acid	7 per cent.
Acetic acid	9 ,,
Propionic acid	12 ,,

These percentages almost exactly correspond to their relative molecular weights, and consequently to their relative saturating power of bases.—*Journal of Physiology*, xvii., No. 5.

EWART JOHNSTONE'S WAY TO PREPARE NITRIC OXIDE.

By MASUMI CHIKASHIGÉ.
Graduate of the Imperial University, Tōkyo, Japan.

In 1882, Dr. Ewart Johnstone announced in the Chemical News (vol. xlv., p. 159) that cobalt nitrate and potassium thiocyanate heated together readily yield nitric oxide. Except by Schertel in the Referate of the *Berichte of the German Chemical Society*, this announcement seems to have been received without criticism, and Michaelis inserted it in his edition of Graham Otto's "Inorganic Chemistry" among the methods of preparing nitric oxide.

The results of my own testing of the method oblige me to conclude that Johnstone is altogether wrong. We are directed by him to mix four parts of a solution of potassium thiocyanate with one part of a solution of cobalt nitrate, such as are ordinarily in use in the laboratory, and gently heat the mixture, when nitric oxide will be copiously evolved. An equation is given of the action, in which four molecules of the potassium salt and one of the cobalt salt appear, and since the quantities to be taken are so indefinitely set down, I started my experiments with these proportions of the salts, both practically in a state of purity. The result proved that in these proportions, as well as in many others which were tried, whether the solutions are dilute or concentrated, only gently heated or freely boiling, nitric oxide is not formed at all by them. Beyond the well-known fact that the mixed solutions are intensely green, no sign of any action was observed. When the solid salts, a little damp, were heated together, also as recommended by Johnstone, watery fusion occurred, and the water boiled off without gas being generated. When, however, the water being gone, the residue got much hotter, there occurred, as might have been anticipated, an explosive reaction in which torrents of gases escaped. These gases, collected over water, and gradually mixed with oxygen, proved to consist of nitric oxide to the extent of about two-thirds of their volume, the rest being principally nitrogen. Carbon dioxide and ammonia were also freely given off, and condensed together to form a sublimate, and a cloud, and a solution in the trough water, of ammonium carbonate or carbamate. The residue smelt strongly of ammonia and was black from the presence of cobalt sulphide, but did not contain the sulphur and the carbon which Johnstone supposed are formed, at least not in quantities which I could detect.

It is a matter of common experience that potassium thiocyanate boiled with dilute nitric acid is decomposed with evolution of nitric oxide and other gases, being partly oxidised and partly converted into the insoluble yellow perthiocyanogen. Now, only a small quantity, or rather only a weak concentration, of nitric acid is needed for this reaction, and the presence or absence of cobalt nitrate makes, I find, no difference. Probably, therefore, Johnstone's laboratory solution of the latter salt contained nitric acid in some quantity, as Schertel, indeed, has suggested.

DECOMPOSITION OF SULPHATES BY AMMONIUM CHLORIDE IN ANALYSIS ACCORDING TO FRESENIUS.

By MASUMI CHIKASHIGÉ.
Graduate of the Imperial University, Tōkyo, Japan.

The accuracy in all respects of Fresenius's standard treatises on Analysis is usually so unimpeachable that it seems proper to call attention to a misleading statement contained in a footnote to § 153 A of the seventh and latest English edition of the "Quantitative Analysis," and also to be found in the earlier editions of this work (4th, 5th, 6th).

Having given in the text the method of separating from magnesium and alkali salts the small quantity of barium left in solution by ammonium carbonate, namely, by adding three or four drops of dilute sulphuric acid, Fresenius states in the footnote to it that the gentle ignition there directed to be made in order to expel ammonium salts, will also effect the removal of any small quantity of sulphuric acid which may remain after precipitating the barium. It is this statement which needs correction.

Even in § 68*a* and § 74*a* of the same work we find enough to cause us to doubt the accuracy of the later statement; for it is there mentioned that magnesium sulphate is not decomposed by igniting it with ammonium chloride, and, on the authority of Rose, that potassium and sodium sulphates, which are decomposable by this treatment, need, for it to be effective, its repeated application at a red heat, inducing effervescence. Obviously such ignition as this is not that gentle ignition directed to be used in § 153, and would entail serious loss of alkali chlorides by spirting and volatilisation. But to place the inaccuracy of the statement in the footnote beyond doubt, I have made a few simple trials of the method.

Magnesia, 0·5 grm., was dissolved in a little hydrochloric acid; to the solution were added two drops of dilute sulphuric acid (1 to 10 water by volume), a solution of about 2 grms. of ammonium chloride, and ammonia in small excess; and the whole was then evaporated to dryness, and all ammonium salts expelled at a barely red heat. Again, a solution of 2 grms. of ammonium chloride was added, and the evaporation and ignition repeated. The residue was dissolved in dilute hydrochloric acid and mixed with barium chloride, which gave a precipitate. On comparing this with that thrown down by barium chloride from two drops of the same dilute sulphuric acid in about the same volume of water, the ignited salts were found to have lost but very little, if any, of their sulphuric acid. The experiment was repeated three times with fresh magnesium chloride, and the same results obtained.

Similar experiments were made with sodium chloride, and no better removal of the sulphuric acid effected than when magnesium chloride was taken.

It is thus quite evident that other steps must be taken to remove sulphuric acid before it is allowable to calculate the weighed alkali salts as chlorides, or to resort to ways of separating magnesia from the alkalis which require the absence of sulphates.

ON THE ACTION OF HYDRAZINE UPON IMIDO-ETHERS.

By A. PINNER and N. CARO.

In two former communications there have been described the manifold, and in part unexpected, products which appear on the action of hydrazine upon benzimido-ether. It has been shown that, according to the proportions and the duration of the reaction occurring at common temperatures, there arise the three compounds—(1) benzenylhydrazine,—

$$C_6H_5.C\begin{matrix}=NH\\ -NH.NH_2\end{matrix};$$

(2) dibenzylhydrazine; (3) diphenyldihydrotetrazin, which latter is oxidised by the oxygen of the air to the deeply-coloured diphenyltetrazin, which if boiled with acids is converted into diphenylisodihydrotetrazin and diphenylbiazoxol. Dibenzylhydrazidin is easily converted at common temperatures by the action of weak acids into diphenyltriazol, whilst ammonia is split off.

Benzenylhydrazidin is instantly converted by nitrous acid into diphenyltetrazotic acid.

The authors have, in a like manner, examined the products obtained by the action of hydrazin upon paratolenylimido-ether.

Among these are *p*-tolenylhydrazidin,—

$$C_7H_7.C\begin{matrix}=NH\\ -NH.NH_2\end{matrix};$$

p-tolenylhydrazidin, with its carbonate, its picrate, and its nitrate.

With aldehyds, tolenylhydrazidine combines easily if its acid solution is heated with the aldehyd whilst water is split off.

Such a compound is benzylidentolenylhydrazidin.

If benzaldehyd is added to a solution of tolenylhydrazidin carbonate, mixed with a little soda-lye, and gently heated, there are formed white prisms of tolenylhydrazidin benzoate, $C_8H_{11}N_3.C_7H_6O_2+H_2O$.

Glyoxalen-ditolenylhydrazidine is formed as a hydrochlorate on boiling an acid hydrochloric solution of hydrazin with a solution of glyoxal-sodium bisulphite.

Nitrous acid acts upon tolenylhydrazidin as upon benzenylhydrazidin, forming instantly tolyltetrazotic acid in a theoretical proportion.

This is a powerful acid which readily decomposes the carbonates. Its salts with the alkalis and alkaline earths are easily soluble, but those with most of the heavy metals are insoluble.

The attempt was made to obtain with this acid an acetyl-compound by boiling with acetic anhydride. There was obtained, however, a mixture of acetyltolylamidine and ditolylmethylkyanidin. It is peculiar that diazobenzol chloride forms with tolenylhydrazidin not the diazobenzol-compound which was expected, but tetrazotic acid perfectly identical with that produced by nitrous acid.

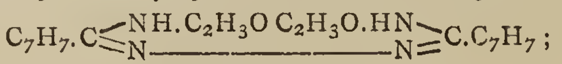
The authors have further obtained and studied benzoyltolenylhydrazidin, phenyltolyltriazol, toluyltolenylhydrazidin, and ditolenylhydrazidin. The last compound crystallises from spirit or from acetone in light yellow leaflets, and is insoluble in water and very difficultly soluble in hot spirit or in acetone.

Its hydrochlorate in a watery solution gradually gives off triazol.

The platinum double salt, $C_{16}H_{18}N_4.H_2PtCl_6$, is obtained by adding platinum chloride to a solution of hydrazin in cold dilute hydrochloric acid. It forms short yellow-red prisms which are completely decomposed if heated beyond 300°.

The double gold salt, $C_{16}H_{18}N_4 2HAuCl_4$, falls at once as a crystalline precipitate if gold chloride is added to a solution of hydrazin in dilute hydrochloric acid.

Diacetyl-ditolenylhydrazidine has the composition—



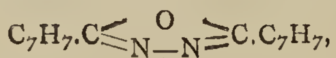
$$C_7H_7.C \begin{array}{l} \diagup NH.C_2H_3O\ C_2H_3O.HN \diagdown \\ \diagdown\!\!\diagdown N \text{——————————} N =\!\!= \end{array} C.C_7H_7\ ;$$

it is formed by boiling a mixture of 1 part ditolenylhydrazidine, 3 parts dehydrated sodium acetate, and 15 parts acetic anhydride, for two hours in a reflux refrigerator, and adding water when cold.

The authors have examined the behaviour of this compound with nitrous acid, and obtained tolyltetrazotic acid, toluyltolenylhydrazidin hydrochlorate, and toluyl-nitrosotolenylhydrazidin hydrochlorate.

From ditolenylhydrazidin ditolyltriazol is easily obtained by the abscission of ammonia.

The authors have also prepared and examined ditolylazol silver, acetylditolyltriazol, ditolyldihydrotetrazin, ditolylisodihydrotetrazin with its double gold salt, ditolylbiazoxol—



$$C_7H_7.C \begin{array}{c} \diagup \quad O \quad \diagdown \\ \diagdown\!\!\diagdown N — N =\!\!= \end{array} C.C_7H_7,$$

and ditolyltetrazin.

A CONTRIBUTION TO THE PHYSICS AND CHEMISTRY OF LIFE IN COLD-BLOODED ANIMALS.

By J. W. SLATER.

It is a fact admitted, but not, I submit, duly appreciated, that in the cold-blooded regions of the animal world we find more varied physical agencies and more multifarious and complicated chemical phenomena than in the hot-blooded forms, *i.e.*, the birds and the mammals.

No species in the two last-mentioned divisions has the power of emitting light, as is done by some fishes, many insects, and marine animalcules. No bird or mammal can use electric currents as weapons for defence or attack, as is done by several fishes, by a bug, and, it is said, by a slug.

Turning to chemical phenomena, we find numbers of arthropoda and a few mollusca endowed with the power of secreting and emitting silk. Nothing of the kind has been recognised among the hot-blooded tribes. Again, in reptiles, amphibia, fishes, insects, and arachnids we observe very generally the secretion of intense poisons, some rapidly fatal if introduced into the circulation of an enemy or a desired prey, and others dangerous only if the animal secreting them is ingested. One offensive poison only occurs in the higher ranks of life: the tarsial spurs of the male Ornithorhynchus are perforated for the emission of a secretion which is slightly venomous. But this can scarcely be called an exception, since the blood of the Ornithorhynchus is colder than the blood of the normal mammals by about 15° F. Neither does the virus of rabies form a true exception, since it is not a normal product but a pathological secretion.

Beautiful as are the colours of many birds, we find in them only one true dye or pigment, the touracine discovered by Prof. A. H. Church in the feathers of the plantain-eater of Africa.

On the contrary, in cold-blooded animals, such as mollusca and insects, dyes abound, and had not attention been drawn to a different quarter by the discovery of the coal-tar colours, they would have been more generally employed and studied.

Some colouring matters of the vegetable world pass over into the cold-blooded animals, but they extend no farther. Such are chlorophyll and tannin, which I have found in many insects, and which is probably the basis of the browns, drabs, greys, and other dull colours so common among Coleoptera. I noticed the occurrence of tannin in papers read before the Entomological Society, and reported in its *Transactions* (1887, p. 32). But I must not omit to state that a variety of tannin had been discovered as early as 1810 by Penant, of Bourgas, in a weevil, *Calandra granaria*, the well-known corn-weevil. As to the occurrence of alizarin in insects, I am doubtful.

As to odours, pleasant or offensive, we must admit that they are not wanting in warm blooded animals. But among cold-blooded forms they are still more abundant and more striking. In certain groups of Coleoptera and Hemiptera their specific odours would be useful in the diagnosis of species, or at least of genera, had we a definite nomenclature for such phenomena.

The question now is whether the energy which in hot-blooded animals is expended in keeping up the temperature of the body is not in the cold-blooded forms converted into luminous or electrical or chemical energy? I would venture to recommend this as a sphere of research for chemists or biologists residing in climates richer in varied animal life.

THE DISTRIBUTION OF THE ORGANIC ELEMENTS.*

By Prof. W. PREYER, M.D., Ph.D.

(Continued from p. 6).

Whereby, except by means of plants in their foods, do fluorine and silicon arrive into the higher animals? The abundance of siliciferous animals (such as the siliceous sponges, &c.) in the sea is evidence of the biological importance of silicon. It serves for strengthening the frame work of animals and plants.

If we search for the presence of elements in living bodies other than the above fourteen, we meet with a great number which may be pronounced certainly absent in plants and animals in free nature. Here belong the heavy metals such as gold and silver, iridium and platinum, ruthenium and osmium, rhodium and palladium, as also the metals of the rare earths from Norway, such as erbium and terbium, samarium, gadolinium, scandium, and yttrium, and a long series of others. It is a matter of course that these elements like all others, as especially arsenic, can be introduced by man into his own body or into that of another animal, as often occurs in medical prescriptions, when *e.g.* preparations of bismuth or mercury are given; but this is here not the question. We must rather ask whether in the free course of nature other than the fourteen elements occur regularly in plants and animals. And this question must decidedly be answered in the affirmative.

Above all it is certain that copper is a constant ingredient of the blood of the Cephalopoda. Copper occurs also in the red pigment of the wing-feathers of the African Touracos and Musophagidæ. Zinc is regularly found in the so-called calamine violets and other plants near zinc works. Aluminium forms often a constituent of the ash of certain lycopods amounting to several per cents. Lithium has been found in tobacco, rubidium in tea and in beets, cæsium in oysters, boron in Italian grapes and melons, iodine and bromine in various marine plants, and manganese in certain muscles.

All these and others have been found not doubtfully but repeatedly, and that by good observers working independently of each other and at different places, probably

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* A Discourse delivered before the General Meeting of the Nassau Association for Natural Science, at Wiesbaden, December 10th 1893.

forming only the beginning of a series of similar facts which will be greatly multiplied in the future.

It would be important to know what is merely accidental in such puzzling occurrences of single elements outside the series in certain plants and animals. As the question now stands it can only be said that, beside the twelve to fourteen vital elements which are universally present in all living beings on the crust of the earth, there are some capable of distinguishing and selecting others which are very abundant or have been locally accumulated.

To these belong iodine, bromine, lithium, boron, zinc, cæsium, rubidium, copper, manganese, aluminium, and perhaps others which I do not mention, as their recognition is not certain.

Hence it appears suitable to separate all the elements contained in living beings into two groups. Those constantly occurring and indispensable are the elements of the first order; those which are not constant, though regularly present in certain vegetable and animal species, are the organic elements of the second order. On the other hand, the elements artificially introduced into the organisms for medical or experimental purposes, or which penetrate into the tissues like lead, tin, &c. (in certain occupations), do not rank among the organic elements, as little as the arsenic consumed by the Styrian arsenic-eaters.

For theoretical examination the elements of the first order are of incomparable greater significance than those of the second, since they are never wanting in living beings; but the collection of facts on the occurrence of other elements in the food of animals and plants is not to be neglected, since thereby our knowledge of the capabilities of living cells is greatly extended. And even if such an observation remains not understood for years or even decennia, its neglect is not admissible. In the meantime the elements of the first order must demand our attention.

What confers upon them the great pre-eminence above all the elements? What renders them alone serviceable for the maintainence of life in all parts of the earth?

More than twenty years ago I pointed out that they have all a small atomic weight. None of them exceeds 56 (iron). The figures are (omitting decimals):—

Hydrogen	1	Nitrogen	14
Carbon	12	Fluorine	19
Oxygen	16	Magnesium	24
Sodium	23	Phosphorus	31
Silicon	28	Chlorine	35
Sulphur	32	Calcium	40
Potassium	39	Iron	56

Hence the fourteen organic elements of the first order rank among the twenty-three elements which have the smallest atomic weights. The meaning of this fact appears at once if we consider that in equal quantities by weight of two kinds of food the greater number of atoms must occur where the constituents have the lowest atomic weights. In the chemism of life—as we shall show in future—the result depends on the effect of many atoms in the smallest space.

Further, the above named organic elements have all a remarkably low specific gravity. If we assign the greatest possible scope to sources of error and defects in the determinations, the specific gravities of the organic elements still remain the smallest, that is for the solid state, water being taken = 1; hydrogen, 0·62 to 0·73 (calculated); carbon, 1·3 to 3·6; nitrogen, 1·2 or slightly above (calculated); oxygen, slightly above 1·1 (calculated); fluorine, slightly above 1·0 (calculated); sodium, 0·97; magnesium, 1·7; silicon, 2·0 to 2·49; phosphorus, 1·82 to 2·34; sulphur, 1·9 to 2·1; chlorine, 1·8 (calculated); potassium, 0·86 to 0·88; calcium, 1·5 to 1·8; iron, 6·9 to 8·0.

Hence only iron, which occurs in living bodies merely in minimal traces, has a high specific gravity.

The meaning of this new fact of the low density of all other essential organic elements is close at hand. If the smallness of the atomic weights proves the great number of atoms in vital chemism, the smallness of the specific gravities points to the high number of molecules which come into action in equal weights. Life is movement and requires easily movable materials, especially gases. Life is metabolism. The most easily motile substances are those with the lowest atomic weight and the lowest specific gravity; consequently those most abundant at the surface of the earth and those most suitable for the maintenance of the vital chemical reactions. If some day the most organic elements became rare, all animals and plants would die of hunger.

The organic elements have further attributes which render them especially suitable for the maintenance of life. They have all a high specific heat, which, taking that of water as = 1, is included within the limits 0·10 and 0·46. That of hydrogen reaches 5·88, whilst all other elements have a specific heat of at most 0·10, and generally much lower down to 0·028.

From the high specific heat of all the organic elements, especially of hydrogen, it follows that all the essential constituents of the tissues of living organisms which are built up of such compounds must have a relatively high specific heat. This inference follows at once from their abundant proportion of water. The biological significance of this fact, as already remarked by Errera, must be sought herein, that living tissues when heat is conveyed to them easily indeed undergoes an increase of its intermolecular movements, but much less easily a rise of temperature than inorganic structures under similar conditions, *e.g.*, the noble metals.

As the constituents of living bodies are almost all bad conductors of heat, they cannot easily share rapid fluctuations of temperature in their immediate neighbourhood—the bark of a tree is a worse conductor than the wood,—and here lies a great advantage especially for all land animals and land plants, whilst in the sea the fluctuations of temperature upwards and downwards are less rapid, and take place within narrower limits than in the atmosphere. All life on the land and in the sea is, indeed, confined within such narrow limits of heat that at the change of the seasons, especially in the temperate zones, without the high specific heat of the organic elements and the small thermic conductivity of the tissues formed of them, many more small and minute organisms would yearly be destroyed by cold than now takes place in the winter.

Besides the physical properties so important for the vital process, the organic elements have further the chemical peculiarity of forming with each other the most numerous combinations and very large molecules, consisting of five, six, or even seven different elements. And these compounds are easily soluble and very readily decomposable, as *e.g.*, hæmatine, which contains in its crystals six elements.

The molecules of albumen, without which life is not conceivable, are very large and are easily decomposed. They are modified by the slighest influences.

This liability of the organic compounds in the living body is certainly the greatest obstacle to its explanation, but in a theoretical point of view it is the most important initial point of the biochemistry of the future.

If we represent to ourselves what, strictly speaking, is alive in the living body, we always arrive at the reply that only the cell contents, the protoplasm, lives, and different as are the opinions on its composition there is no longer any question that it is an extremely complicated structure, and not a "mucoid" or an "albumenoid" structure.

Protoplasm is continually decomposing as long as it is alive. The supply of the material used up in this self-consumption is yielded by the organic elements in the assimilable compounds of the food. But we must not imagine that the dissimilation of the entire series of the kataplastic chemical process ensue in the same manner as the imitations of the metabolic processes attempted in the laboratory. However many components of living animals and plants we produce by artificial synthesis, we have not proved even in a single case that the living body proceeds in the same manner. With decompositions the case is identical. How the organism forms the carbonic acid which it evolves is unknown, and yet there is absolutely no life without the formation of carbonic acid! The reason why this problem has not yet been found capable of solution lies doubtless in our insufficient knowledge of the nature of the place where the formation of carbonic acid takes place. That the foci of oxidation lie exclusively in the protoplasm is certain, but what is their aspect?

As protoplasm has an extremely complicated structure, recognised only of late since the improvement of the microscope, in which the very minute interstices and meshes, often at the very limit of visibility and not even permanent, but altering under the very eyes of the observer, the question arises whether in so peculiar a locality chemical reactions can altogether take place in the ordinary manner. An examination of the conditions necessary for the completion of any chemical reaction has shown that one of the most important of these conditions, the action of mass, cannot be realised in living protoplasm on account of the smallness of the open spaces. The chemical equilibrium can here be reached only to a very restricted extent. But then the chemism of the living cell-contents, the chemism of protoplasm, *i.e.*, the inter-reaction of the very unstable compounds of the organic elements, must be another, and lead to other results than in test-glasses and retorts. Even the extremely fine division of every minutest particle of nutriment which is burnt in millions and millions again of different places in the organism, and then especially the strikingly externally measurable average temperature of the focus of combustion, render it probable that, in the narrow interstices of living protoplasm, it is no longer the large molecules but the atoms which rush together in the moment of their liberation.

It is not the ordinary chemical reactions in which enormous numbers of molecules forming masses enter into action at the same place, but atomistic reactions which here come into play, single combats of atoms in the nascent state with strong unsatisfied affinities, and nowhere in an exactly identical manner, since the protoplasms, like organisms, are individually different.

Thus the more accurate determination of the properties of vital compounds of organic elements in connection with the scrutiny of the minutest structure of vegetable and animal protoplasm, promises to throw a clear light on the foundation of all life, the biochemical processes.

DISPLACEMENT OF CARBON BY BORON AND SILICON IN CAST-IRON DURING FUSION.

By HENRI MOISSAN.

The study of the solubility of carbon in different metals, or in the same metal at temperatures more and more elevated, has led us to examine what might be the action of boron and silicon on a given iron carbide maintained in the liquid state.

The action of boron upon iron has not yet been studied, or, at least, in the experiments made on this question the boron has not been detected after the experiment in the metal submitted to its action. As regards the action of silicon, no experiment has been conducted in a methodical manner. It has long been known in siderurgy that cast metals are the poorer in carbon the richer they are in silicon; but the action of silicon upon cast-iron has not yet been studied with precision.

Cast-iron in fusion is a liquid in which, as we are about to show, the reactions are sometimes as definite as in the aqueous solution treated in our laboratories at the ordinary temperature. The complexity of certain cast-irons which may contain a great number of compounds as impurities alone renders the reactions more complicated.

Action of Boron upon Grey Cast-Iron.—We set out with a grey cast metal from St. Chamond containing 3·8. of total carbon and 0·5 scoriæ. Ten grms. of this metal were placed in a lined porcelain boat with 2·5 grms. of boron. The whole was strongly heated in a reverberatory furnace in a porcelain tube filled with dry hydrogen. After the experiment we found in the boat a regulus well fused and covered with a black felt formed entirely of graphite. The metal had a yellowish tint, and presented on its surface some long prisms well crystallised. It contained 8 to 9 per cent boron. It was a borated cast metal mixed with iron boride partly crystallised.

This borated cast metal contained only 0·27 per cent of carbon, and gave no scoriæ on the combustion of the residue in oxygen.

Boron, therefore, easily combines with the impurities of the cast metal, and carries them off in the slags. With the iron oxide existing in solution in the metal it plays a part analogous to that which Troost and Hautefeuille have ascribed to manganese.

We may therefore conclude from this reaction that the boron has expelled the carbon in the proportion of 1 to 10, and at the same time eliminated the substances which form the slag.

This experiment was repeated four times with another specimen of grey cast metal from St. Chamond containing 3·24 carbon and 0·418 of scoriæ. After the action of the boron the following figures were obtained:—

	1.	2.	3.	4.
Carbon	0·36	0·28	0·17	0·14
Scoriæ	0·02	0·00	0·03	0·01

We then substituted a white refinery metal from the blast furnace of Saint-Louis, at Marseille. This cast metal contained 3·85 carbon and 0·36 of scoriæ. After the experiment it contained only 0·24 carbon and 0·06 scoriæ.

We have varied the form of the experiment, not allowing a great excess of boron to act upon the liquid metal. We melted at the forge 500 grms. of grey cast metal from St. Chamond, and when perfectly liquid we added 50 grms. of a borated cast metal containing 10 per cent of boron. After agitation the crucible was covered and the heating terminated. At the moment when the borated metal was added to the grey metal it remained for some time on the liquid bath and was dissolved only on agitation.

When cold the ingot obtained had a laminated aspect. It was very hard, resisting the graver, and having the appearance of a white casting.

By the action of boron the proportion of carbon in this metal was reduced from 3·75 to 2·83. The boron had therefore displaced carbon, a portion of which was recovered in the state of graphite between the metallic regulus and the crucible.

Displacement of Carbon by Silicon.—We repeated the same experiment, heating some fragments of grey cast metal in a lined boat with the powder of crystalline silicon. The silicon under these conditions expels the carbon, which is found as graphite above the metal. But, as we remarked at the outset, a cast metal produced in the blast furnace is a very complex compound.

We have repeated the experiment under more simple conditions.

We first prepared in the electric furnace a cast metal, rich in carbon, from soft iron and the charcoal of sugar. We then threw upon this liquid bath some grammes of melted silicon in globules. When cold the ingot, smooth on its upper surface, had the aspect of a silicated cast-iron with a white, brilliant fracture. It contained very little combined carbon and no graphite. But in the midst of the regulus there appeared a great cavity filled with graphite brilliant and well crystallised.

Conclusions.—Boron and silicon distinctly displace carbon in cast-iron or in melted iron carbide. These substances when maintained at a sufficient temperature behave exactly like aqueous solutions of certain compounds in which we can precipitate or displace this or that substance present in solution or combination.

If the displacement of carbon is not absolutely complete this fact is due to the formation of an equilibrium between the iron silicide and carbide, an equilibrium the conditions of which vary with the temperature and the impurities contained in the bath.—*Comptes Rendus*, cxix., No. 26.

SOME RECENT CONTRIBUTIONS TO OUR KNOWLEDGE OF METALLIC REDUCING AGENTS.*

By H. F. KELLER.

(Concluded from p. 9).

Group III.

The main group embraces boron, aluminium (scandium), yttrium, lanthanum, and ytterbium, and gallium, indium, and thallium, form the sub-group. Three atoms of magnesium are required to abstract the oxygen from their oxides:—

$$R_2O_3+3Mg=3MgO+2K'''$$

Phipson has observed that boric acid is reduced upon ignition with magnesium. With the aid of magnesium, boron was also obtained by Geuther from the boro-sodium fluoride, and quite recently L. Gattermann has shown that boric acid as well as borax can be reduced by means of this metal, so as to yield products which are suitable for the preparation of various volatile boron compounds.

Winkler confirmed these observations. He states that the trioxide and the borate of sodium are easily reduced, the latter with much energy and evolution of sodium vapour. But he found that, instead of free boron, the residue contains magnesium boride of variable composition; for, on treatment with hydrochloric acid, boron hydride is given off as a gas. Sometimes a solid residue remains, which is likewise a compound of boron and hydrogen.

Owing to the acid-forming character of boron, the reduction was never complete; borates, upon which magnesium has no action, are always formed.

An attempt was also made to prepare a boron suboxide by limiting the supply of magnesium, thus:—

$$B_2O_3+Mg=2BO+MgO,$$

but no indication of such an oxide was observed.

A dark coloured product resulted from heating alumina with magnesium. The reaction appeared to be quite energetic; the mass exhibited a vivid glow and increased largely in volume. In addition to finely divided aluminum, a new oxide, AlO, and magnesium spinel had been formed. This monoxide could not be obtained in a pure condition, but its existence was proved beyond doubt. It is best prepared by heating in a current of hydrogen a mixture corresponding to—

$$Al_2O_3+Mg=2AlO+MgO.$$

This oxide is a brownish-black voluminous powder, is pyrophoric, and liberates hydrogen slowly from water; it precipitates cuprous oxide from copper sulphate solution, and is exceedingly susceptible to oxidation.

Winkler suggests that the blue colour of sapphire, and possibly also that of ultramarine, may be due to a small proportion of this monoxide.

Of the rare earths of group III., only yttria and lanthana were subjected to the action of magnesium. The energy of the reduction appeared to increase with the atomic weights.

Upon the oxides of the sub-group magnesium reacts with great violence; the intensity of reduction has its maximum in In_2O_3.

The behaviour of Tl_2O_3 towards magnesium appears to be an exception. Before the temperature of reduction is reached, this oxide splits up into Tl_2O and O_2, and the thallous oxide so formed is then only partially reduced. Thallium carbonate, however, is deprived of its oxygen completely, and with explosive violence.

Group IV.

The most interesting results perhaps were obtained in the fourth natural group of elements.

The known properties of carbon, silicon, titanium, zirconium, cerium, and thorium assign them positions in the main group, while germanium, tin, and lead constitute the sub-group.

In addition to their acid-forming dioxides, the majority of these elements are capable of giving monoxides. It was therefore deemed desirable to attempt not only the complete reduction of the higher oxides, but also a *partial* removal of the oxygen with a view to procure the lower oxides.

The statements of different experimenters concerning the action of carbon dioxide upon magnesium are somewhat conflicting.

That a ribbon of the metal will burn in an atmosphere of carbon dioxide was first observed by Kessler, but neither he nor other chemists who repeated and modified his experiment explained satisfactorily the nature of the reaction.

Winkler shows in the first place that magnesium, when *moderately* heated in a current of carbon dioxide, does not take fire, but is slowly converted at its surface into a carbide, carbon monoxide being formed at the same time. Upon increasing the heat to a full redness, the metal was inflamed and continued to burn with a dazzling light. The products of this combustion are magnesia and carbon.

When the magnesium is employed in the form of powder, these reactions take place even more readily. At a temperature considerably below a red heat carbon monoxide appears, and its quantity is greatly increased when low redness is reached. The metal burns with great brilliancy at a full red heat, and unless the current of carbon dioxide is very rapid, its reduction is complete.

It has already been mentioned that a separation of carbon was observed when magnesium acted upon carbonates; also that carbon monoxide was formed when an excess of the carbonate was present. Further experiments were made with calcium carbonate. A mixture of this substance with magnesium: $CaCO_3+3Mg=$ $=Ca+C+3MgO$, heated in a current of hydrogen detonated violently. The examination of the débris revealed the presence of a carbide of magnesium. No metallic calcium was observed in the residue when only two atoms of magnesium were used for each molecule of the carbonate.

According to Kessler burning magnesium is extinguished in carbon monoxide, while Parkinson asserts that at a red heat the metal burns vividly in this gas. Both observations were found to be correct. A spiral of magnesium wire ignited in the air, ceased to burn while introduced into a jar of carbon monoxide, but when strongly heated in a current of the gas the magnesium emitted light, and a grey coating of a carbide appeared on its surface.

Numerous experiments to determine the exact composition of this carbide were made, but without yielding a definite result.

Silicon exhibits a pronounced tendency to combine

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* *Journal of the Franklin Institute*, October, 1894.

with magnesium. Silicon-magnesium was first observed by Wöhler in 1858.

The reduction of silica by metallic magnesium was observed in 1864 by Phipson, and Parkinson showed in 1867 that silicon-magnesium, as well as a magnesium silicate, are formed at the same time. A few years ago L. Gattermann published an interesting paper in which he showed how very easily silicon dioxide is reduced by magnesium. He states that either silicon or silicon-magnesium can be obtained by varying the proportion of magnesium; and he applies the reaction to the preparation of volatile compounds of silicon, such as the chloride, bromide, iodide, silicoformic acid, silico-chloroform, &c.

Gattermann and Winkler agree that an energetic reaction occurs upon heating a mixture of one molecule of silica and two atoms of magnesium.

$$SiO_2+2Mg=Si+2MgO.$$

By adding magnesia to the mixture the heat of the reaction was moderated, but it was then found that much silicon-magnesium was contained in the product. If the reaction be effected at low temperature and in the presence of an excess of magnesium, silicon-magnesium is always formed, while at a high heat or in presence of magnesium, only amorphous silicon results.

A silicon monoxide could not be obtained by the reduction of silica, either by magnesium or silicon.

Many silicates are reduced quite as easily as the dioxide; in some cases the metallic base is likewise reduced, *e.g.*, potash glass.

None of the oxides studied presented greater difficulties than titanium dioxide. The results may thus be summed up:—Titanium dioxide was not reduced to the metallic state; a mixture of monoxide and a titanium spinel were the products of the reaction. Other intermediate oxides were sometimes formed. When the residue was treated with hydrochloric acid HTi_3O_4 was formed, which upon heating gave TiO_2 and hydrogen. Neither titanium-magnesium nor a titanium hydride was observed.

The reduction of zirconia was effected by heating it with magnesium to a high temperature. A monoxide could not be identified with certainty; and $ZrMg_2$ does not appear capable of existing.

According to the amount of magnesium employed either cerium or Ce_2O_3 were obtained from cerium dioxide. An intermediate monoxide was not formed. The reduction begins at a moderate red heat and is accompanied by a vivid glow. A considerable proportion of the magnesium is volatilised. In the nascent state cerium was found to absorb hydrogen in large quantities.

The formation of a metallic hydride at a bright red heat is a most remarkable observation. It is clearly proved to be correct by the following experiment.

A mixture is prepared according to the equation:—

$$CeO_2+2Mg=Ce+2MgO.$$

Twenty grms. of this mixture are placed in a combustion tube through which a current of dry hydrogen is passed, while a gentle heat is applied to expel any moisture. The further end of the tube is then closed with a strong clip. Hydrogen is allowed to enter the other end and the heat quickly raised to bright redness; a rapid current of hydrogen is seen to pass through the wash-bottles into the tube.

The hydride is of a brownish-red colour. It is without action on water at ordinary temperatures, but sets free hydrogen upon heating. Hydrochloric acid dissolves it to $CeCl_3$, with evolution of hydrogen. It was found impossible to completely remove magnesia from the product. The hydride is very inflammable, and detonates with potassium chlorate, potassium nitrate, &c.

The analytical results obtained point to the formula CeH_2.

After the existence of a cerium hydride had thus been established, the thought suggested itself that the other elements of group IV. might possibly be capable of forming similar compounds. Only carbon and silicon were known to form hydrides, but these elements could not be made to unite with hydrogen when their oxides were reduced by magnesium. Since titanium could not be reduced to the metal, it is not strange that all efforts to form a hydride gave negative results; zirconium and thorium did absorb hydrogen and yielded hydrides similar to CeH_2. The same was observed with lanthanum, and this led Winkler to believe that this element belongs to the cerium group; but he showed subsequently that yttrium and other trivalent elements, and even the divalent barium, strontium, and calcium can unite with hydrogen.

These hydrides represent a new class of metallic compounds, in which only half the usual valence of the metals is satisfied.

The action of magnesium upon chlorides has been made the subject of an elaborate research by Seubert and Schmidt.

I must content myself with a very brief statement of some of the main results obtained by these chemists.

Both the anhydrous bodies and the aqueous solutions of the chlorides were subjected to the action of magnesium.

In the former case the substance, either mixed with magnesium powder or conducted over it in the form of vapour, was heated to a high temperature. It was found that all chlorides could thus be reduced to the metallic state, but the reduction was incomplete in the groups of the metals of the alkalies and the metals of the alkaline earths.

In *neutral* aqueous solutions all the metallic chlorides, save those of the alkalies and those of the alkaline earths, gave up their chlorine to the magnesium. In some cases the metals were deposited in the metallic state (silver, gold, thallium, lead, arsenic, antimony), but in most cases hydroxides were precipitated. These hydroxides always represent the lowest state of oxidation. $CuCl_2$, *e.g.*, is changed into Cu_2O; chromium, aluminum, iron, manganese, cobalt, and nickel, all yielded hydroxides.

It would seem that the tendency to form such hydroxides is peculiar to the positive metals, and especially to those forming basic salts. Seubert and Schmidt believed this to be due to a dissociation of the chlorides into hydroxides and hydrochloric acid. They suppose, for instance, that an aqueous solution of $AlCl_3$ contains $Al(OH)_3,3HCl$. This view is rendered quite probable by the fact that solutions of copper, nickel, cobalt, and chromium exhibit the colour of their *hydrated* salts.

Of other metals whose oxides possess a high heat of formation aluminum has found some application in the reduction of oxides. Beketow has employed it with success to prepare some of the metals of the alkalis; and the experiments of Greene and Wahl of reducing manganese oxides by means of metallic aluminum are still fresh in our memory.

I am convinced that a continued study of the relative affinities of the metals for oxygen and other negative elements, will lead to important applications in metallurgy, and give new and valuable methods to synthetic and analytical chemistry.

Extraction of the Free Acids of Bees-wax.—T. Marie—The purity of cerotic acid is ascertained by the following means:—Fractionated crystallisation of the acid in ordinary ether. Fractionated precipitations by magnesium acetate. Fractionated crystallisations of the methylic and ethylic ethers in ordinary ether. From the residue from the above treatment melissic acid is extracted by repeated treatments with methylic alcohol. Crude cerotic acid contains from 30 to 40 per cent of homologous acids.—*Bull. de la Soc. Chim. de Paris.*

ON THE TECHNICAL ANALYSIS OF ASPHALTUM.*

By LAURA A. LINTON.

(Concluded from p. 11).

A second set of experiments was then tried in which cold turpentine and carbon disulphide were used as solvents of asphaltene. The results obtained for samples 1 and 2 were as follows:—

No.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
1.	32·54	20·3435	12·368	34·6775	99·929
2.	25·049	54·53	2·441	17·9215	99·9415

The experiment was now made of somewhat varying the method of treatment for the following reasons:—First, because of the difficulty of dissolving out the asphaltene while on the filter by simply allowing the solvent to run through it, and secondly, because, in consequence of the high specific gravity of petroleum ether, a considerable portion of sand or other mineral matter mixed with asphaltene always adhered to the flask, thus necessitating a separate determination of this portion. The method now employed for the removal of petrolene and asphaltene was the decantation method, and the solvents used for asphaltene were hot turpentine and chloroform.

The samples were digested over-night in petroleum ether; in the morning the solution containing the petrolene was, as far as practicable, removed from the flask, and the remainder was evaporated over a steam bath; after weighing, the residuum containing the asphaltene was digested in hot turpentine over the steam-bath, and finally, the whole contents of the flask were poured upon a balanced filter and treated as in the first experiments.

The percentage composition of Nos. 1, 2, and 17, as determined by the decantation method, was as shown in the following table;—

No.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
1.	31·51	22·9865	11·4195	34·073	99·989
2.	25·055	52·245	5·758	16·918	99·962
17.	64·571	21·2545	13·706	0·3613	99·8928

In carrying out this method a great many determinations were lost, due to the fact that, in evaporation to dryness over the steam bath, the contents of the flask were in part bumped out. In consequence, this method was soon abandoned as impracticable, and finally, funnels with stop-cocks were employed, in which the contents of the filter could be digested. Boiling hot instead of cold turpentine was used, and when necessary the digestion was continued over-night, and all the after washings were made with hot turpentine. Numerous trials showed that carbon disulphide dissolves little more than hot turpentine. The last trace of asphaltene, insoluble in either turpentine or carbon disulphide, was removed by chloroform.

In order to determine the relative solvent power of hot turpentine, carbon disulphide, and chloroform, the following method of qualitative analysis was applied to the 23 samples enumerated above. From a half grm. to one grm. of the material was digested over night in a four-ounce Erlenmeyer flask with about 50 c.c. of petroleum ether. Next morning the contents of the flask were poured upon a filter, and the undissolved residue washed with petroleum ether until the filtrate was no longer coloured. Boiling spirits of turpentine was then poured upon the filter until it passed through colourless, when carbon disulphide was used in the same manner, followed lastly by chloroform. The action of the successive solvents is shown in the accompanying table (see next page).

Of the twenty-three asphaltes examined, there was not one that did not yield some asphaltene on treatment with chloroform; consequently, it is safe to infer that in the analysis of asphaltes, unless final washing be made with chloroform, the per cent of asphaltene will be too low. There was a marked difference observed in the different asphaltes as to the manner in which their constituent asphaltene was dissolved on treatment with hot turpentine. In Nos. 4, 5, 6, and 7, and a few others, the asphaltene dissolved out in a few minutes, while in the case of others, notably No. 15, it was a matter of hours, and even of days, before every trace soluble in turpentine could be removed. No. 9 seems to be an asphaltic freak, as it contains no petrolene whatever, and is insoluble in both hot turpentine and carbon disulphide, while chloroform and amylic alcohol dissolve but the slightest trace.

It was a difficult matter to determine the relative quantity of asphaltene dissolved by the different menstrua, as the only guide used was the colour of the filtrate. This suggests a most interesting research—the fractional, quantitative determination of asphaltene.

From my experience in the analysis of asphaltes, I would advise that a preliminary qualitative analysis be always made of each new variety of asphaltum before any quantitative determinations are attempted, care being taken to observe the behaviour of different asphaltes with the different solvents. This method of procedure is to be recommended, not only because it would prove an economy of time and reagents used, but also because, in this way, much would be learned concerning the nature of petrolene and asphaltene.

A trial was made with Cuban asphalte to determine the solvent power of petroleum ether (87° Beaumé) as compared ,with that of California naphtha (74° Beaumé) and ethyl ether with the following results:—

Sample.	Solvent for Petrolene.	Per cent of Petrolene.
No. 2.	Petroleum ether	25·8516
,, ,,	California naphtha	32·444
,, ,,	Ethyl ether	32·5455

The high percentage of petrolene when California naphtha or ethyl ether are used indicates that the asphaltene is, in part, dissolved, and consequently, that these menstrua cannot be used as solvents of petrolene in the determination of asphaltes.

In selecting a method for the quantitative analysis based upon the results of these experiments, it is assumed that, until a strictly scientific method is worked out, the present empirical determination of petrolene and asphaltene will continue in use. The three considerations of economy, speed, and convenience will together control the selection. So long as the significance of the difference between the 25·8 per cent dissolved by petroleum ether and the 32·5 per cent dissolved by ethyl ether is an unknown element in the problem—that is, whether it be 7 per cent of petrolene or of asphaltene that is involved—it is better to use petroleum ether, because it is cheap and easily obtained of a uniform quality. So, too, it is better to use boiling hot turpentine followed by chloroform as solvents of asphaltene, and thus rid ourselves of carbon disulphide altogether.

With these considerations in view the following method of analysis is recommended:—

Weigh two suitable portions in 4-oz. Erlenmeyer flasks, and 50 c.c. of petroleum ether, cover, and allow to stand over night. The following morning decant the liquid upon a balanced filter placed within a 3-in. funnel provided with a stop-cock in the neck. Add another portion of petroleum ether to the flask, allowing two or three hours for digestion, and decant the liquid upon the same filter as before; this process is to be continued until the liquid ceases to be coloured, then transfer the whole of the bitumen to the filter. Dry the flask in a steam-bath and weigh; any increase in weight of the flask should be subtracted from the amount determined

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* *Journal of the American Chemical Society*, xvi., No. 12.

Sample No.	Hot Turpentine.	Carbon disulphide.	Chloroform.
1.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
2.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a perceptible amount.
3.	Dissolves nearly all.	Dissolves a trace.	Dissolves a trace.
4.	,, ,, ,,	Dissolves the slightest trace.	Dissolves the slightest trace.
5.	,, ,, ,,	Dissolves a trace.	Dissolves a perceptible amount.
6.	,, ,, ,,	,, ,,	,, ,, ,,
7.	,, ,, ,,	Dissolves the slightest trace.	Dissolves the slightest trace.
8.	,, ,, ,,	,, ,, ,,	Dissolves a trace.
9.	Dissolves nothing.	Dissolves nothing.	,, ,,
10.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
11.	,, ,, ,,	,, ,,	,, ,, ,,
12.	,, ,, ,,	,, ,,	,, ,, ,,
13.	,, ,, ,,	,, ,,	,, ,, ,,
14.	,, ,, ,,	,, ,,	,, ,, ,,
15.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.
16.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
17.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.
18.	,, ,, ,,	,, ,, ,,	,, ,, ,,
19.	Dissolves nearly all.	Dissolves a trace	Dissolves a perceptible amount.
20.	,, ,, ,,	,, ,,	,, ,, ,,
21.	,, ,, ,,	,, ,,	Dissolves a trace.
22.	Dissolves a large amount.	Dissolves a considerable amount.	,, ,,
23.	,, ,, ,,	,, ,, ,,	Dissolves a considerable amount.

as petrolene. Wash the filter and its contents with petroleum ether, place these with the filter counterpoise in a steam-bath, dry, and weigh; the loss in weight of the bitumen represents the petrolene.

Rinse the flask thoroughly with boiling turpentine and add the liquid to the filter in the closed funnel, pour upon the filter a sufficient quantity of boiling turpentine to wholly submerge it, cover and allow the digestion to continue for several hours or over night. Repeat the digesting and filtering with boiling turpentine until the filtrate becomes colourless. The filter should be much smaller than the funnel. Rinse the flask with chloroform and pour upon the filter, add sufficient chloroform to wholly submerge the filter and allow at least an hour for digestion; wash with chloroform until the filtrate passes through colourless, then dry and weigh; the loss in weight represents the asphaltene. The filter is now to be burned in a platinum crucible and, if the asphaltum be combined with limestone, the residue re-carbonated with ammonium carbonate, dried in a steam-bath, and weighed, the loss in weight represents the organic matter not bitumen, or coke, in the case of artificial asphaltic residuum, produced by heat.

There is necessity for washing the flask with the different solvents, not only because the petroleum ether is too light to rinse out all of the mineral matter, but also because some of the asphaltene adheres to the flask. Generally the turpentine removes all of the mineral matter, as well as part of the asphaltene, but if it does not, then after the flask is rinsed with chloroform it must be again dried and weighed, and the increase in weight added to the weight of the mineral matter in the platinum crucible. If water be present the asphalte should be dried in a steam-bath to a constant weight before being digested in petroleum ether. It is possible that some natural asphaltes might experience a trifling loss of volatile oils at the temperature of the steam-bath, but in most instances such loss would be too slight to be regarded. With care and patience this method has been found capable of yielding very closely concordant duplicate results at each step.

The table (see next col.) exhibits the results of a number of quantitative analyses made according to this method.

While this research is in no sense complete—it has, in fact, but opened up a wide field for further work—yet, sufficient evidence has been obtained to show that petrolene and asphaltene are not substances, but empirical terms that designate mixtures of substances soluble under certain conditions in different menstrua.

Sample. No.	Water.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
1.	2·029	32·4455	22·1115	8·1215	35·2865	99·994
2.	0·3911	25·4605	54·414	2·469	17·0305	99·7651
4.	—	35·087	63·183	1·7285	—	99·9985
					Not recarbonated.	
5.	—	8·518	3·924	25·791	61·764	99·997
6.	—	7·486	4·316	—	88·198	100·
7.	—	8·786	3·267	—	87·947	100·
8.	—	3·349	2·4215	—	94·228	99·9985
12.	0·335	11·323	3·81	1·124	83·407	99·999
15.	—	49·959	50·041	—	—	100·
17.	—	64·571	21·2545	13·706	0·3613	99·8928
18.	—	63·498	29·966	6·095	—	99·559
19.	—	4·387	2·831	4·102	88·65	99·97
20.	0·434	6·666	1·87	3·697	87·33	99·997
21.	—	66·788	31·932	1·278	—	99·998

It is not unfair to assume that in these empirical mixtures, so long known under the names of petrolene and asphaltene, the lower members of all the different groups of hydrocarbons now known may be found. Again,—just as some petroleums, which are varieties of bitumen, consist chiefly of paraffins—notably Pennsylvania petroleum—and some, like Russian petroleum, consist of the additive benzenes, while still others contain mixtures of the two, is it not reasonable to presume that solid bitumens, like liquid bitumens, are equally variable in composition? If this be the case, then it is equally fair to assume that any solvent taken will not dissolve substances of identical composition from different asphaltes.

A review of the results here given suggests the query, Have the methods heretofore employed for the technical analysis of asphaltum really been analytical at all? Would not a method and process suggested by the results of the qualitative analyses given in this paper and based on the successive application of different solvents and yielding results similar to those of fractional distillation really become analytical, especially if the separate portions dissolved by the different solvents were subjected to such treatment by oxidising agents as would enable us by a comparison of the products of oxidation to determine to what groups of hydrocarbons the different substances dissolved respectively belong?

I take pleasure in hereby acknowledging my indebtedness to the courtesy of the Hon. Thos. R. Bard, President of the Union Oil Co., of California, for the use of the laboratory of the company while engaged in this research.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 25, December 17, 1894.

The meeting of December 17th being the yearly public session of the Academy was taken up by the Presidential Address commemorating the discoveries of the year, and eulogising the members lost since the last annual session.

This discourse was followed by the announcement of the prizes awarded.

Half the Jecker Prize was awarded to M. Barbier for his numerous and important researches in organic chemistry. Portions of this prize have also been assigned to P. Adam and M. Meslans, the latter of whom has been successfully engaged in the study of the organic fluorides.

Two Montyon Prizes for protective improvements in the insalubrious arts have been awarded to A. Balland for his sanitary researches on wheats, flours, and bread, and M. Layet for his treatise on industrial hygiene.

The Cuvier Prize is this year awarded to John Murray, one of the naturalists of the *Challenger* Expedition, and the editor of its records.

A list was then given of the prizes offered for researches in future years. The Jecker Prize of 10,000 francs will be awarded next year for the most important progress in organic chemistry.

The Vaillant Prize for a study of the physical and chemical causes which determine the existence of the rotatory power in transparent bodies has been postponed to 1896.

A prize of 100,000 francs is offered for a remedy which will cure Asiatic cholera in an immense majority of cases, or for a detection of the causes of the disease, and for a certain prophylactic agent.

A general condition to be observed by all candidates for the prizes offered by the Academy is that the portion of their researches which they submit to the decision of the Academy must be sent in on or before June 1st of the year in which the prize is to be awarded.

Zeitschrift für Anorganische Chemie, Vol. vii., Part 4.

Nitrogen Trioxide (Nitrous Anhydride).—G. Lunge and G. Porschnew.—The authors, briefly collating their results, conclude that nitrous anhydride is readily formed below −21° at the ordinary pressure from nitrogen peroxide and nitric oxide, and appears as a pure indigo-blue liquid. It is stable at the above temperature, but on a rise of temperature decomposition sets in and is completely or nearly complete on its passage into a state of vapour. The properties of the above mixture of components are, as regards any third substance, perfectly identical with those of N_2O_3 in a state of vapour.

Contributions to the Chemistry of Cerium.—L. M. Dennis and W. H. Magee.—Already inserted.

Simple Preparation of Hydrogen Phosphide.—J. W. Retgers.—If red phosphorus is placed in a glass tube and a current of dry hydrogen is allowed to pass over it, the gas escaping is merely pure hydrogen. But if the part of the tube where the phosphorus lies is heated with a gas flame, the bubbles of the gas, if allowed to escape through water, are found spontaneously inflammable.

Constitution of the Zeolites.—F. W. Clarke.—This paper does not admit of useful abstraction.

Part 5.

Constitution of the Cobalt, Chromium, and Rhodium Bases.—S. M. Jörgensen.—In this communication the author discusses the preparation and constitution of the aquotetramminxantho cobalt salts, and of those of the dinitrotriammin cobalt salts.

Double Chlorides and Bromides of Cæsium, Rubidium, Potassium, and Ammonium with Trivalent Iron, also a Description of two Ferro-ferric Double. Bromides.—P. T. Waldon.—The ferro-ferric salts in question are—

$$RbBrFeBr_2.2FeBr_33H_2O$$
$$\text{and } KBrFeBr_22FeBr_3,3H_2O.$$

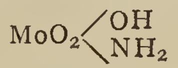
On Colloidal Silver.—E. A. Schneider.—Inserted in full.

On Solutions of Metallic Silver.—Carey Lea.—The results lead us to the view that the solutions of silver are colloidal. The solubility, however, is perfect, so that the solutions bore the same tests of solubility as the solutions of crystalloids.

Triammonium Orthophosphate and the Qualitative Detection of Magnesium.—P. Schottländer. If in testing a solution for magnesium we use ordinary ammonium phosphate (1 : 10) instead of sodium phosphate, we may, in the total absence of magnesium, obtain a finely crystalline precipitate which is deceptively similar to magnesium-ammonium phosphate, and may thus easily lead to error. This is especially the case if such ammonium chloride and strong ammonia have been added, additions well known for promoting the separation of magnesium.

Thorium Meta-oxide and its Hydrates.—James Locke.—The author concludes that the composition of meta thorium oxide corresponds to the formula Th_3O_5. The meta-thorium hydroxide has the composition $Th_3O_5H_2O$.

Molybdenum Amides.—Hermann Fleck and E. F. Smith.—The author recognises the existence of a monamide—



$$MoO_2\begin{cases}OH\\NH_2\end{cases}$$

The molybdenyl group (MoO_2) is evidently not capable of retaining two amido groups so as to form a stable product like $MoO_2(NH_2)_2$. Its existence, if at all possible, is of very brief duration. The same may be maintained of amido-molybdic acid, $MoO_3.OH.NH_2$.

Action of Phosphorus Trichloride upon Magnesium Nitride.—E. A. Schneider.—The possibility of producing a phosphorus nitride in a pyrogenous way seems not probable. The affinity of nitrogen to phosphorus at elevated temperatures is very slight.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 106.

This issue contains no chemical matter.

Royal Institution.—On Tuesday next (Jan. 15) Professor Charles Stewart, M.R.C.S., will deliver the first of a course of twelve lectures at the Royal Institution on "The Internal Framework of Plants and Animals." On Thursday (Jan. 17), Mr. William S. Lilly, M.A., will begin a course of lectures on "Four English Humourists of the Nineteenrh Century"; and on Saturday (Jan. 19), Mr. Lewin F. Day will deliver the first of three lectures on "Stained Glass Windows and Painted Glass (from the Point of View of Art and Craftsmanship)." The Friday Evening Meetings of the Members will commence on January 18th, when a lecture will be delivered by Prof. Dewar on "Phosphorescence and Photographic Action at the Temperature of Boiling Liquid Air."

MISCELLANEOUS.

Determination of the Proportions of Calcium Carbonate and Magnesium Carbonate in Soils, Ashes, &c.—Albert Trubert.—We know that 1 c.c. of a normal solution of nitric acid or hydrochloric acid decomposes 50 m.grms. of calcium carbonate or 42 m.grms. of magnesium carbonate, setting at liberty 22 m.grms. of carbonic acid, occupying at 0°, and at the pressure of 750 the vol.—

$$\frac{22}{1{\cdot}977746} = 11{\cdot}12377 \text{ c.c.}$$

and forming at the same time nitrates or chlorides soluble in water. This reaction enables us to determine the total weight of the calcium and magnesium carbonates present in a given weight of earth, and consequently the weight of each carbonate. We attack a weight, p, of the dried earth with dilute hydrochloric acid, and find the volume V of the carbonic gas produced at the temperature t and the pressure H. We then calculate the corresponding volume V_0 of dry carbonic acid at 0° and at the pressure 760. On dividing V_0 by 11·12377, we obtain the number N of c.c. of the normal acid solution necessary to convert the insoluble carbonates entirely into soluble salts. We then take the same weight, p, of dry earth, and add N c.c. of the normal acid solution. We filter when there is no longer any further effervescence (the transformation is complete when a violet colouration is produced in presence of a drop of normal soda solution and of phenolphthalein). We wash the residue, dry completely, and weigh. Let p' be the weight obtained; the difference $p-p'$ gives the total weight p' of the carbonates contained in p of dry earth. We may thus calculate the proportions of calcium carbonate and magnesium carbonate. *First Method.*—Let x be the volume of carbonic acid at 0° and 760 produced by the unknown weight of calcium carbonate; let y be that produced by the magnesium carbonate. We have (1) $V_0 = x + y$. The weight of the calcium carbonate is in m.grms., $x \times 1{\cdot}977746 \times \frac{50}{22} = 4{\cdot}4948\, x$. That of the magnesium carbonate is $y \times 1{\cdot}977746 \times \frac{42}{22} = 3{\cdot}7756\, y$. We have then (2) $p_1 = x \times 4{\cdot}4948 + y \times 3{\cdot}7556$. If we replace y by its value taken from (1), we have—

$$x = \frac{p_1 - 3{\cdot}7756\, V_0}{0{\cdot}7192}.$$

Consequently the weight c of the calcium carbonate is (3) $c = 6{\cdot}2497\, p_1 - 23{\cdot}5963\, V_0$. We have then the weight m of magnesium carbonate by difference or by the formula $m = 23{\cdot}5963\, V_0 - 5{\cdot}2497\, p_1$.—*Comptes Rendus*, cxix., No. 24.

A Survival.—According to the *Chemiker Zeitung*, there exists—or did in 1890—the last of the alchemists, who, for a consideration in hard cash, is prepared to teach the art of converting copper into gold. In his letters, which are written in very bad German, the adept informs us that from 1 lb. of copper, new or old, he can produce 1 grm. of fine gold. The *Chemiker Zeitung* also calls attention to two new inventions for washing and bleaching, &c. "Polysulphine," the newest detergent, consists, according to Dr. Kreis, the chemist of the Canton Bâle, of—Water, 26·9 per cent; sodium carbonate, 70·5; sodium chloride, 0·55; combined sulphur, 0·59; free sulphur, 0·85. "Ammonin," placed on the market by a Heidelberg firm, as "crystalline ammonium sulphide," consists of the lime mud from the Leblanc soda manufacture, dried and ground! It is recommended by some disinterested experts as a "distinguished bleach and detergent."

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

County Analyst.—Could you tell me what are the usual qualifications for a borough or county analyst, or for an analyst in a chemical works? I am anxious to commence a course of study with some such end in view.—W. D.

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Society of Arts, 8. (Cantor Lectures). "The Arc Light," by Prof. Silvanus P. Thompson, F.R.S.
—— Medical, 8.30.
TUESDAY, 15th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
—— Institute of Civil Engineers, 8.
—— Pathological, 8.30.
WEDNESDAY, 16th.—Society of Arts, 8. "Commercial Synthesis of Illuminating Hydrocarbons," by Prof. Vivian B. Lewes.
—— Meteorological, 8. (Anniversary).
—— Microscopical, 8. (Anniversary).
THURSDAY, 17th.—Chemical, 8. "Acid Sulphate of Hydroxylamine," by Dr. Divers, F.R.S. "Mercury and Bismuth Hypophosphites," by S. Hada. "Kamala—Part III.," by A. G. Perkin.
—— Royal Institution, 3. "Four English Humourists of the Nineteenth Century," by W. S. Lilly, M.A.
—— Society of Arts, 4.30. The Lushais, and the Land they Live in," by Capt. John Shakespear.
—— Royal Society Club, 6.30.
FRIDAY, 18th.—Royal Institution, 9. "Phosphorescence and Photographic Action at the Temperature of Boiling Liquid Air," by Prof. Dewar, F.R.S.
—— Quekett Club, 8.
SATURDAY, 19th.—Royal Institution, 3. "Stained Glass Windows and Painted Glass," by Lewis F. Day.

THE CHEMICAL NEWS.

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THE
COMMERCIAL SYNTHESIS OF ILLUMINATING HYDROCARBONS.*

By Professor VIVIAN B. LEWES,
Royal Naval College, Greenwich.

The two methods most used in chemical science for tracing the changes taking place in matter, and determining the composition of bodies, are, firstly, breaking up compounds into their ultimate constituents, a process which is called "analysis"; and, secondly, by building up the compound from the elementary matter which forms it, a process to which the name of "synthesis" has been given.

If we take chalk and heat it in the lime-kiln, or in the chemist's crucible, a heavy colourless gas, called carbon dioxide, escapes from it, and leaves behind a substance which we know as quicklime. If, now, this quicklime be further acted upon by chemical methods, the metal calcium and the elementary gas oxygen can be obtained from it, whilst the carbon dioxide when collected can be decomposed into the elements carbon and oxygen, and by such a series of operations as this we might perform the analysis of chalk.

If now we start with the metal calcium, with carbon, and with oxygen, it is perfectly simple to reverse the operation, and rebuild the chalk molecules from these elementary forms of matter; by burning the carbon and calcium respectively in oxygen, we obtain the quicklime and the carbon dioxide, and by bringing these substances together in the presence of moisture, chalk or calcic carbonate is once more formed, and we have synthetically built up the chalk from its constituents.

By such simple methods as these most inorganic compounds can be synthetically produced from elementary matter, but in the so-called organic chemistry it is not so easy to employ such constructive methods for the formation of compounds, and up to the end of the first quarter of this century it was supposed that organic bodies were only produced as the result of animal and vegetable life, and that their formation was due to the so-called "vital force," which was credited with governing all changes taking place in living organisms.

In 1828, Wöhler showed that urea could be formed from cyanate of ammonium, whilst, later on, Fownes made cyanogen by the direct combination of carbon and nitrogen, these two discoveries taken together proving the possibility of forming an organic product from inorganic materials, and after this point had been reached, and the possibility of applying synthetic methods to the production of organic bodies had been demonstrated, compound after compound was built up without the aid of either vegetable or animal life, and the barrier between inorganic and organic chemistry finally broken down. Cases, however, in which such methods could be commercially successful were few and far between, as in most cases the processes which had to be adopted were costly and laborious.

In all the phenomena of ordinary combustion which we employ to provide us with heat and light, there are no compounds of greater interest than the class of organic bodies which, being formed of carbon and hydrogen in various proportions, have been termed hydrocarbons, and it is to this class of bodies that all the gases which can be used as ordinary illuminants owe their luminosity. Amongst the hydrocarbons, the simplest compound is acetylene, in which two atoms of carbon are united with two atoms of hydrogen; and it has long been known that if a stream of hydrogen is passed through a globe in which the voltaic arc is produced between carbon points from a sufficiently powerful current, this gas is produced in minute quantities. It can also be formed in small quantities by the decomposition of carbon tetrachloride in the presence of hydrogen by the induction spark, whilst it is produced during processes of checked combustion in hydrocarbon flames.

The direct combination of carbon and hydrogen in the electric arc is a true case of synthesis, and if we could form acetylene in this way in sufficiently large quantities, it would be perfectly easy to build up from the acetylene the whole of the other hydrocarbons which can be used for illuminating purposes. For instance, if acetylene be passed through a tube heated to just visible redness, it is rapidly and readily converted into benzol; at a higher temperature naphthalene is produced, whilst by the action of nascent hydrogen on acetylene, ethylene and ethane can be built up. From the benzol we readily derive aniline, and the whole of that magnificent series of colouring matters which have gladdened the heart of the fair portion of the community during the past five-and-twenty years, whilst the ethylene produced from acetylene can be readily converted into ethyl alcohol, by consecutively treating it with sulphuric acid and water; and from the alcohol, again, an enormous number of other organic substances can be produced, so that acetylene can, without exaggeration, be looked upon as one of the great keystones of the organic edifice, and, given a cheap and easy method of preparing it, it is hardly possible to foresee the results which will be ultimately produced.

From acetylene we can produce all those bodies which we are accustomed to look upon as the most important ones in our coal-gas, and which, up to the present time, have never been produced from anything but coal, hydrocarbon oils, or other organic matter undergoing destructive distillation; but it has often occurred to those of us who are interested in the manufacture of illuminating gas, that as the supply of coal gets smaller, and as oil in time begins to share the same fate, from what sources are our illuminants and our fuels to be obtained; and in my mind, at any rate, the synthetic production of hydrocarbons has long been a day dream, which I, however, never expected to see possible on a commercial scale.

Not only was the synthetic production of acetylene in the electric arc well known, but ever since water-gas has been introduced, small traces of acetylene and methane have been found in it under conditions which render it impossible that they should have been produced from any compound present in the incandescent fuel, and which must have been due to the direct combination of carbon and hydrogen, but these traces only occurred in quantities so small as rarely to amount to one per cent, and it was manifest that the production of the compounds could not take place in large quantities under influences which would immediately tend to decompose them.

In 1836 it was found that when making potassium by distillation from potassic carbonate and carbon, small quantities of a by-product, consisting of a compound of potassium and carbon, was produced, and that this was decomposed by water with liberation of acetylene; whilst Wöhler, by fusing an alloy of zinc and calcium with carbon, made calcic carbide, and used it as a source from which to obtain acetylene by the action of water.

Nothing more was done until 1892, when Maquenne prepared barium carbide by heating at a high temperature a mixture of barium carbonate, powdered magnesium, and charcoal, the resulting mass evolving acetylene when treated with water; whilst, still later, Travers made calcic carbide by heating together calcic chloride, carbon, and sodium. None of these processes, however, gave any commercial promise, as the costly nature of the

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* A Paper read before the Society of Arts, Wednesday, Jan. 16, 1895.

potassium, sodium, or magnesium which had to be used made the acetylene produced from the carbide too expensive.

It is now some twenty-five years ago since I listened to one of the Friday evening lectures at the London Institution, given by Mr. Greville Williams, and in the same way that the thread of some melody lingers in one's mind, so has the concluding sentence of that lecture constantly recurred with ever-increasing force—"The impossible is a horizon which recedes as we advance; and the *terra incognita* of to-day will to-morrow be boldly mapped upon every schoolboy's chart"; and the haunting dream of the possibility of synthesising hydrocarbons commercially has, with the onward march of science, today become an accomplished fact.

As is so usual in the history of discovery, the factor which has endowed us with the power of doing this was not the outcome of an elaborate research, having this discovery for its ultimate goal, but was found by chance during the search for another object.

Whilst working with an electric furnace, and endeavouring by its aid to form an alloy of calcium from some of its compounds, Mr. T. L. Wilson noticed that a mixture containing lime and powdered anthracite, under the influence of the temperature of the arc, fused down to a heavy semi-metallic mass, which having been examined and found not to be the substance sought, was thrown into a bucket containing water, with the result that violent effervescence of the water marked the rapid evolution of a gas, the overwhelming odour of which enforced attention to its presence, and which, on the application of a light, burnt with a smoky but luminous flame.

Investigation into the cause of this phenomenon soon showed that in a properly constructed electric furnace, finely ground up chalk or lime, mixed with powdered carbon in any form, whether it were charcoal, anthracite, coke, coal, or graphite, can be fused with the formation of a compound known as calcic carbide, containing 40 parts by weight of the element calcium, the basis of lime, and 24 parts by weight of carbon, and that, on the addition to this of water, a double decomposition takes place, the oxygen of the water combining with the calcium of the calcic carbide to form calcic oxide or lime, whilst the hydrogen unites with the carbon of the calcic carbide to form acetylene, the cost of the gas so produced bringing it not only within the range of commercial possibilities for use *per se*, but also the building up from it of a host of other compounds, whilst the production of the calcic carbide from chalk and from any form of carbon renders us practically independent of coal and oil, and places in our hands the prime factor by which Nature in all probability produces those great underground storehouses of liquid fuel upon which the world is so largely drawing to-day.

Wonderfully and intensely interesting as is the train of thought opened up by the discovery of this substance and its commercial production, the object I have in view this evening is not to discuss theoretic possibilities, but to show you the important effect which it will have in the direction of our great gas industry, and the phase of this which I wish to deal with specially is the value of acetylene, either for producing *per se* an enormously high illuminating effect, or for the enrichment of low grade coal-gas.

When the calcic carbide is placed in a glass flask, and water allowed to slowly drip upon it from a dropping tube, the decomposition at once commences with considerable rapidity, and the acetylene pours off in a continuous stream. As the decomposition continues, the solid mass in the flask swells up, and is eventually converted into a mass of slaked lime.

Calcic carbide is a dark grey substance, having a sp. gr. of 2·262, and, when pure, a pound of it will yield on decomposition 5·3 cubic feet of acetylene. Unless, however, it is quite fresh, or means have been taken to carefully protect it from air, the outer surface gets slightly acted upon by atmospheric moisture, so that in practice the yield would not exceed 5 cubic feet. The density and hardness of the mass, however, protects it to a great extent from atmospheric action, so that in lumps it does not deteriorate as fast as would be expected, but in the powdered condition it is rapidly acted upon.

For commercial purposes the carbide will be cast direct from the electric furnace into rods or cylindrical cartridges, which, when 12 inches long and 1¼ inches in diameter, will weigh one pound and will give 5 cubic feet of gas.

The acetylene so made, when analysed by absorption with bromine, the analysis being also checked by determining the amount present by precipitation of silver acetylide, gives 98 per cent of acetylene and 2 per cent of air and traces of sulphuretted hydrogen, the presence of this impurity being due to traces of sulphate of lime—gypsum—in the chalk used for making it, and to pyrites in the coal employed.

Acetylene is a clear colourless gas with an intensely penetrating odour which somewhat resembles garlic, its strong smell being a very great safeguard in its use, as the smallest leakage would be at once detected; indeed, so pungent is this odour that it would be practically impossible to go into a room which contained any dangerous quantity of the gas.

This is an important point to remember, as the researches of Bistrow and Liebreich show that the gas is poisonous, combining with the hæmoglobin of the blood to form a compound similar to that produced by carbon monoxide, whilst the great danger of the latter gas is that having no smell its presence is not detected until symptoms of poisoning begin to show themselves, so that no fear need be apprehended of danger from this source with acetylene.

Acetylene is soluble in water and most other liquids, and at ordinary temperature and pressure—60° F. and 30 inches of mercury—ten volumes of water will absorb eleven volumes of the gas, but as soon as the gas is dissolved the water being saturated takes up no more. Water already saturated with coal-gas does not take up acetylene quite so readily, whilst the gas is practically insoluble in saturated brine—100 volumes of a saturated salt solution only dissolving 5 volumes of the gas. The gas is far more soluble in alcohol, which at normal temperature and pressure takes up six times its own volume of the acetylene, whilst 10 volumes of paraffin under the same conditions will absorb 26 volumes of the gas. It is a heavy gas, having a specific gravity of 0·91.

When a light is applied to acetylene it burns with a luminous and intensely smoky flame, and when a mixture of 1 volume of acetylene with 1 volume of air is ignited in a cylinder a dull red flame runs down the cylinder, leaving behind a mass of soot and throwing out a dense black smoke. When acetylene is mixed with 1·25 times its own volume of air, the mixture begins to be slightly explosive, the explosive violence increasing until it reaches a maximum with about twelve times its volume of air and gradually decreases in violence until, with a mixture of 1 volume of acetylene to 20 of air, it ceases to be explosive.

The gas can be condensed to a liquid by pressure, Andsell finding that it liquefied at a pressure of 21·5 atmospheres at a temperature of 0° C., whilst Cailletet found that at 1° C. it required a pressure of 48 atmospheres, the first-named pressure being probably about the correct one. The liquid so produced is mobile and highly refractive, and when sprayed into air the conversion of the liquid into the gaseous condition absorbs so much heat that some of the escaping liquid is converted into a snow-like solid which catches fire on applying a light to it, and burns until the solid is all converted into gas and is consumed.

In my researches upon the luminosity of flame, I have shown that all the hydrocarbons present in coal-gas and other luminous flames are converted by the baking action taking place in the inner non-luminous zone of the flame into acetylene before any luminosity is produced, and that it is the acetylene which, by its rapid decomposition at 1200° C., provides the luminous flame with these carbon particles, which, being heated to incandescence by various causes, endow the flame with the power of emitting light. The acetylene being in this way proved to be the cause of luminosity, one would expect that in this gas we have the most powerful of the gaseous hydrocarbon illuminants, and experiment at once shows that this is the case.

Owing to its intense richness it can only be consumed in small flat-flame burners, but under these conditions emits a light greater than that given by any other known gas, its illuminating value calculated to a consumption of 5 cubic feet an hour being no less than 240 candles.

Illuminating Power of Hydrocarbons for a Consumption of 5 cubic feet of Gas.

	Candles.
Methane	5·2
Ethane	35·7
Propane	56·7
Eythelene	70·0
Butylene	123·0
Acetylene	240·0

Having arrived at this startling result, it will be as well to at once turn to the commercial aspect of the problem, as it is upon this that the utilisation of this magnificent illuminant is entirely dependent. At the present time information from America shows that calcic carbide can be produced at a little under £4 a ton, and the beautifully pure lime obtained by the decomposition would be worth to the gas manager about 10s. a ton, and as a ton of the carbide will give rather more than 1¼ tons of quicklime or 1¾ tons of slaked lime, £3 10s. may be taken as the cost of the acetylene produced from a ton of the material, and will leave a margin for handling. A ton of the carbide will yield in practical working 11,000 cubic feet of acetylene, which will bring the cost of the gas out at 6s. 4½d. per 1000.

The cheapest and best enrichment process known at the present time is that introduced by Mr. Young, and which has been adopted at a number of gas works in Scotland and the north of England. In this process, by special methods of retorting, oils are decomposed to yield a rich gas, which, in the photometer, and burnt in suitable burners *per se*, gives an illuminating value of about 60 candles, but for which an enrichment value of 96 candles is claimed.

I am desirous of understating rather than overstating the powers of the acetylene, so that, instead of taking enrichment values for it which might be questioned, I prefer to simply take the illuminating power of the gas when burnt, *per se*, and the light measured in the photometer, which, as before stated, is 240 candles, whilst, for the same reason, we will take the claimed enrichment value of the Young gas instead of its photometric value.

An extended experience, gained with the Young process, as used at St. Helens for the enrichment of coal-gas, shows that the cost may be taken at 3s. 4d. per 1000 cubic feet. If now we compare this with the acetylene at 6s. 4½d. per 1000, we find that the 240-candle gas at this price would be equal to Young gas at 2s. 6½d. Moreover, the Young plant, to work a ton of oil per diem, costs —according to the experience at Peebles—£1500, and generates 22,000 cubic feet a day, the retorts for this purpose occupying a very considerable space, whilst, to make the same volume of acetylene, two tons of material would have to be handled, and the whole operation could easily be carried out in one small egg-ended boiler, fitted with an automatic water feed and automatic gas delivery valve to outlet of the main for the holder, so that the enriching gas could be added *pro rata* to the gas as it left the works in order to bring it up to any required strength in the same way as is done with the Maxim-Clarke enrichment, and all the troubles of stratification in the holder would be done away with. For the first few hours the water in the consumers' meters would absorb small quantities of the acetylene, but quickly becoming saturated, no further absorption would take place.

It is well known that acetylene forms two compounds with ammoniacal solutions of the metals silver and copper, and both of these compounds, when dry, can be readily exploded by percussion, friction, or heat. In the early days of gas supply copper pipes were used in New York, and Torrey in 1839 found in them a brown scaley deposit, which exploded when struck or heated to 200°C., and which was in all probability acetylide of copper.

An extended series of experiments on this point show that when metals are kept in the gas, even if moisture be present, no action takes places unless water condenses on the metal, when tarnishing with silver and copper, and to a less degree with brass, commences, and under these conditions an acetylide of mercury can also be formed, but the other metals remain unacted upon. If, therefore, iron, tin, lead, or compo pipes be used for the gas supply, no precautions are necessary. Copper and brass tubes must either be coated inside with some varnish not acted upon by the acetylene, or tin lined.

In America, which was the birthplace of this method of making calcic carbide, the acetylene is mixed with an equal volume of air, and the mixture burnt at small slit burners; but I confess to a grave mistrust of this method of using the gas, as the margin of safety in the amount of air required to convert the mixture into an explosive is so small that the danger of exceeding it on any large scale must be very great, as any mistake or alteration in the mixing apparatus used for this purpose might easily bring the percentage of air up to the explosive limit, whilst the diluting action of the nitrogen of the air reduces the illuminating value of the acetylene present from 240 candles to 130.

The possibility of liquefying acetylene by pressures not far exceeding those at which liquid carbon dioxide is produced so largely, enables enormous volumes of this gas to be compressed into the liquid state in small wrought iron or steel cylinders, and in this condition, by means of suitable reducing valves and burners of the right construction, it may be stored and burnt. Used in this way it will be of the greatest possible value for floating buoys, and the small cylinders can also be arranged in the form of portable lamps, whilst for use in the country, where no gas is available, a large cylinder of the liquid gas placed in an outhouse would supply a country house with light for a very long period; and there is no doubt that there is a very great field for it in this direction, as by utilising suitable burners a consumption of half a cubic foot an hour will give a light equal to from 20 to 25 candles.

Perhaps the most valuable suggestion which has been made with regard to the utilisation of this remarkable method of making acetylene is that advantage should be taken of the method of preparation to utilise the body for making portable lamps for dining and drawing-rooms in places where no gas supply exists. To do this a strong steel cylinder, 4 inches in diameter and 16 inches in length, is fitted with an opening in the top of such size that a pound cartridge or stick of the calcic carbide can be passed through it. The cylinder has a second opening at the bottom, closed by a screw, for cleaning out the lime left by the decomposition. The right proportion of water is put into the cylinder, and the stick of carbide, coated with a slowly soluble glaze, is inserted and the head of the lamp screwed on. This head contains a double reducing pressure valve, which brings down the pressure existing in the cylinder to that necessary for the proper consumption of the gas, it also being fitted with a valve. As the glaze dissolves from the surface of the stick of carbide, acetylene is generated, and the five cubic feet are compressed by their own pressure, the cylinder being stood in a vessel of cold water whilst the gas is generating, and the gas can then be burned from a suitable jet at the rate of half a cubic foot per hour, which will give a light of over 20 candles for something like ten hours. When the gas is all burnt out from the cylinder, the top of the lamp is screwed off, and the bottom plug also removed, and the lime washed out from the interior of the cylinder by a rapid stream of water, and re charged as before. Used in this way also, this gas would rapidly replace oil-gas for railway lighting, as the fittings at present in use for the Pope and Pintsch systems would answer perfectly well for the purpose of using acetylene, the only difference being that the cylinder placed below the carriage, which, under the present conditions, is filled with compressed oil-gas, would be utilised, not only as a storing, but as a generating vessel for the acetylene, the highly expensive oil-gas manufacturing and pumping plant being done away with, and a magnificent illumination ensured in the carriage.

Of late years an idea has been slowly permeating the minds of some gas managers in this country that it might be well to adopt a dual gas supply, one for fuel purposes, which would consist of a poor coal-gas of about 12 candles, whilst the gas for illuminating purposes would be of about 20 candles; and in one town at least it has been proposed and, I believe, carried out that a supply of poor quality coal-gas should be sent out during the day, when the maximum consumption is for heating purposes, and a richer gas at night for illuminating purposes, utilising the same mains for both. Although this is possible in a small town where the area to be supplied is not large, it would be impossible in a big town where many miles of huge mains have to be travelled before certain districts are reached, and the cost of a double set of mains would render a dual supply an impossibility.

The use of acetylene would render it possible for the gas company to send out a 12-candle gas for heating purposes, both by night and day, whilst a small enrichment cylinder might be attached to the gas outlet pipes from the consumer's meter, and which would be made to automatically enrich the gas supplied to his house, so that by setting a valve he could have any quality he might desire.

The economic value of an illuminant such as acetylene becomes apparent when we compare the cost of the gas for equal illumination with the light obtained from other illuminants. The London gas has an illuminating power of 16 candles, whilst the acetylene has an illuminating value of 240 candles, and this, at 6s. 9½d. per 1000, would in light-giving value be equivalent to London coal-gas at less than 6d. per 1000.

In order to obtain a given illumination, moreover, the volume of gas to be consumed is excessively small, as compared with any other illuminating gas, and the products of combustion are reduced to an excessively low limit. One hundred cubic feet of London coal-gas will yield 50 cubic feet of carbon dioxide and 140 cubic feet of water vapour as the products of its complete combustion, whilst 100 cubic feet of acetylene would yield 200 feet of carbon dioxide and 100 feet of water vapour. The acetylene, however, in its combustion gives a light of 240 candles, as against 16 yielded by the coal-gas; and for equal illumination, therefore, the amount of carbon dioxide and water vapour produced is enormously smaller.

The following table contrasts the products of combustion evolved from London coal-gas when consumed in various forms of burners, and giving an illumination of 48 candles, which may be presumed to be the amount of light required in a fair-sized London dining-room, and contrasted with this is the amount of the products of combustion which acetylene would evolve in giving the same amount of light; whilst to make the meaning clearer, I have added the number of adults who would exhale the same amount of carbon dioxide in the same time.

Burner.	Gas consumed.	Carbon dioxide produced.	Adults.
Flat flame, No. 6 ..	19·2	10·1	16·8
Flat flame, No. 5 ..	22·9	12·1	20·1
Flat flame, No. 4 ..	25·3	13·4	22·3
London Argand ..	15·0	7·9	13·1
Acetylene..	1·0	2·0	3·6

If we obtained the same amount of light from paraffin lamps, the carbon dioxide evolved would be equivalent to 22·5 adults; whilst as far as carbon dioxide goes, you might as well invite 32·7 more guests to dinner as use 48 sperm candles to supply the needed illumination.

The flame of acetylene, in spite of its high illuminating value, is a distinctly cool-flame, and in experiments which I have made by means of the Le Chatelier thermo-couple, the highest temperature in any part of the flame is a trace under 1000° C., whilst with coal-gas burning in the same way in a flat-flame burner, the temperature rises as high as 1360° C., whilst if the heating effect of the flames be contrasted for equal illumination, it will be seen that the acetylene flame has so small a heating effect, considering its area, that it would not be much greater than the ordinary electric incandescent lamp.

The intensity of the light will make small acetylene lamps of enormous value for lantern projection, for railway signals, and, coming down to smaller things, bicycle lamps; whilst I should imagine the ease of production specially adapts it for such purposes as lighthouse illumination.

The scope and possibilities of such a discovery as that which I have brought before you this evening cannot be realised until many factors, at present unknown, are thoroughly worked out, and you must remember also that the time at my disposal has only enabled me to bring before you to-night some factors connected with the light-giving value of this hydrocarbon, and that, as a stepping-stone to the synthesis of other bodies, its value will be incalculable; and one cannot help feeling that, as science grows, and as our grasp and comprehension of the marvellous processes by which Nature builds up her matter become more and more extended, synthesis may have even greater conquests to make than the mere building up on a commercial scale of an illuminating hydrocarbon.

We are beginning to realise more and more fully the marvellous way in which Nature keeps matter in circulation, the way in which animal and vegetable structures are built up from the simplest and most plentiful substances, and the way in which, when the structure is done with, those processes of slow combustion which we call decay again convert the waste bodies into carbon dioxide and water vapour, from which once more Nature reconstructs the vegetable and animal kingdon; and it may be that as our perception of the methods of that marvellous natural architecture gets clearer and keener, we may discover how, by simple synthetic processes, the carbon dioxide and water vapour, which form Nature's building material, may be synthetically utilised by us in building up, not the perfected form of man, or animal, or plant, but the building on a commercial scale of the food which is required by Nature for carrying on the functions necessary for life.

ON THE

HYGROSCOPIC CHARACTER OF IODINE AND ON THE DETERMINATION OF ITS MOISTURE.

By C. MEINECKE.

Pure iodine, absolutely dry, spread out flat in a porcelain capsule, but protected from dust, was exposed for a considerable time to the action of the air in the laboratory. From time to time the quantity of water taken up was determined indirectly; the iodine thus exposed being compared volumetrically with pure iodine which had been preserved in air-tight glasses.

The experiments proved that iodine is not changed by the absorption of water in the course of a few hours. Even after five days it had lost very little of its iodometric value. After three weeks the difference reached nearly 0·06 per cent. Hence the attraction of water from the air by iodine is very slightly perceptible.

In a second series of experiments, iodine, recently sublimed, was placed under a bell along with a capsule of water, and compared from time to time with dry iodine.

The experiments showed that even pulverulent iodine can take up only about 0·1 per cent of moisture even under the condition most favourable for attracting water, and which can only be produced artificially. Iodine in leaflets, in well-preserved crystals, can condense on its surface only 0·05 per cent of water. In presence of sulphuric acid moist iodine loses all its water.

Meinecke determined the water in iodine in the following simple manner :—The iodine to be examined he lets fall from a weighing-glass into a dry test-tube of about 1 c.m. in width and 6 c.m. in length, superstratifies it then with at least four or five times the quantity of ignited silver-powder, closes the tube with a glass stopper ground to fit, and weighs either at once, or if the action of the iodine on the silver has been aided by a rise of temperature, complete cooling. The tube is then opened, placed in a small beaker, and heated on an asbestos plate so gently, that the formation of silver iodide takes place very slowly. The temperature can be regulated in case of need by removing the beaker from the plate. With a little experience the process may be so conducted that mere traces of iodine escape. Should such an escape really occur it is at once indicated by the change in the colour of the silver iodide. The silver powder then appears attached to its surface, whilst with correct management the upper layers of the silver should remain unchanged. During the formation of the silver iodide the escaping water is condensed on the colder parts of the tube, from which, after the complete absorption of the iodine, it may be expelled by the application of heat. When this has been effected the tube is stoppered, allowed to cool, and weighed. The difference shows the quantity of water which was present in the iodine. The determination with the preparatory operations requires scarcely an hour.

The author has applied the method both to dry iodine and to such as had been moistened by the addition of small weighed quantities of water.

The author's analysis show that the indirect determination of water is quite accurate. But the method can be combined, either weighing by absorption, by means of a tube ground to fit the desiccation tube, and containing calcium chloride or phosphoric acid, into which the escaping water may be driven by the application of gentle heat.

The method is trustworthy even if the iodine contains chlorine and bromine, but not if cyanogen is present, as cyanogen iodide is then liable to be volatilised.—*Chemiker Zeitung.*

CONTRIBUTIONS TO VOLUMETRIC ANALYSIS.*

By B. REINITZER.

Preparation and Use of Pure Sodium Carbonate as Original Standard for Acidimetry and Alkalimetry.

AMONG the many substances which have been proposed as original standards for acidimetry and alkalimetry pure sodium carbonate, originally proposed by Gay-Lussac, still remains in almost exclusive use. It is not merely especially suitable from its chemical nature, but meets in an eminent degree the demands to be made upon an original standard.

It is easily obtained in a state of almost chemical purity; it can be weighed without difficulty, and on exposure to a moderate temperature not restricted by any narrow limits it assumes the composition expressed by its formula, so that the chemical effect corresponding to a weighed quantity can be calculated with complete certainty. It has a rather high molecular weight, so that errors in weighing are of the less importance. As the initial material for the preparation of pure sodium carbonate there is used of course sodium hydro-carbonate (bicarbonate), which is met with in commerce in a very pure state, and which is converted into sodium carbonate by a moderate heat not reaching ignition.

If the bicarbonate is contaminated with alkaline chlorides or sulphates it can be easily freed from these impurities by washing with small quantities of distilled water (See Fresenius, "Quantitative Analysis," sixth edition, vol. ii.). At present we find in commerce bicarbonate contaminated with insoluble solids. If we dissolve from 10 to 15 grms. of such a product in hot distilled water there quickly settles to the bottom of the vessel a larger or smaller quantity of a heavy, black, finely-granular powder, which on closer examination is found to consist of iron oxides. Contamination with fine woody fibres is also not uncommon. It will now be shown how from such a bicarbonate contaminated with insoluble matter, and in addition with small quantities of the above mentioned soluble alkaline salts, a perfectly pure sodium carbonate free from insoluble matter may be easily and quickly obtained. About 250 c.c. of distilled water are heated in a tall beaker (preferably of Jena apparatus glass) to 80°, and, whilst constantly stirring, sodium bicarbonate is added in small portions as long as it dissolves at the temperature mentioned. In consequence of the decomposition of the bicarbonate a part of the carbonic acid escapes with so violent effervescence that if the space is insufficient a part of the liquid flows over. However, not one-half, but about one-third, of the total carbonic acid is liberated, yielding ultimately a solution containing 1 mol. sodium hydrocarbonate to 1 mol. sodium carbonate. As soon as further portions of bicarbonate added no longer dissolve, the liquid is filtered into a flask, preferably through a folded filter in a hot-water funnel. The flask is cooled in a jet of water down to 10—15°. An abundance of a coarsely crystalline salt is quickly deposited. This salt is a mixture of bicarbonate with artificial trona, a double salt of the composition—

$$Na_2CO_3+NaHCO_3+2H_2O.$$

It is separated from the mother-liquor (containing along with much trona the small quantities of soluble impurities contained in the bicarbonate) by drainage, suction, and washing with cold distilled water.

In consequence of the coarse crystalline texture of the precipitate the use of a paper filter is quite unnecessary. The glass funnel is closed below with a small Bunsen funnel of strong sheet platinum. Thus we entirely prevent the precipitate being contaminated with paper fibres without danger of its passing through even on the strongest suction. After prolonged drainage the precipitate is repeatedly washed with *small quantities* of *cold* water, which are poured upon the precipitate from a beaker, rapidly and at once, so that the entire mass is kept uniformly moist. According to well-known practice the liquid must be sucked completely off before pouring in a fresh quantity of water.

As the commercial bicarbonate contains only traces of chlorides and sulphates, a few drenchings of water suffice for the production of a perfectly pure salt. The washed salt is now transferred with a platinum or horn spatula to a platinum capsule and heated to a redness scarcely visible by daylight. When cold it is ground up and heated again in the same manner.

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* *Zeitschrift Angewandte Chemie.*

The sodium carbonate thus obtained is quite pure, and even large quantities (20 to 30 grms.) dissolve in water without any trace of turbidity. If we work in beakers of ordinary glass it may occasionally happen that the soda yields a solution not quite clear, but slightly opalescent.

The safest method would be of course to effect the solution of the carbonate in platinum or silver vessels of a sufficient depth. Perhaps nickel vessels, which are now easily procured, might be used with advantage.

In any case we obtain a quite faultless product if we work in beakers of Schott's glass, which resists chemical action much better than ordinary apparatus glass. The yield of pure soda with the proportions above mentioned is 37 per cent of the quantity obtainable by simply heating the bicarbonate employed. If the water used for dissolving the bicarbonate is heated to 100° the yield is smaller, about 22 per cent, and the danger of obtaining a product contaminated with the constituents of the glass is greater.

As pure sodium carbonate slowly attracts water from the air, it should be heated immediately before use. To avoid over-heating and decomposition we proceed as follows:—The powder is placed in a thin-sided porcelain crucible and spread in a thin layer on the sides of the crucible by pressure with a horn spatula. As the powder becomes slightly adhesive by pressure it is easy to produce a uniform thin coating of the sides of the vessel, that is to line the crucible with soda. If we then heat the soda shrinks away from the sides of the crucible and forms a thin-sided soda crucible, the sides of which are pervaded by the heat with uniform rapidity and ease. The heating can of course be effected in a platinum crucible, but we must then be more cautious, lest sintering and fusion of the soda occur, attended with a loss of carbonic acid. This method of heating in a thin layer is also adopted for determinations of moisture in salts much better than the common method in which the expulsion of the water from the interior of the saline mass in the crucible is practicable only if the outside is over-heated.

The salt is then ground up whilst still hot, and filled into a weighing bottle. The quantity of soda required for the primary standard is then approximately measured out of the weighed glass with a horn spoon, and the glass is weighed again. To avoid loss the soda is filled in over a dry funnel inserted into the flask to be used for titration. The horn-spoon is left in the funnel, and both are rinsed into the flask with hot water. Cold water causes the soda to adhere together into a hard lump, which resists the action of the acid for a long time. In hot water the soda remains pulverulent and dissolves quickly. This manner of weighing out and transferring has advantages as compared with the customary method of shaking out of a tube. No powder remains adhering to the neck of the tube which occasions losses or the absorption of moisture, and there is no danger of introducing too much or too little of the soda into the flask. The weighing bottle after being grasped in the hand must be allowed to stand on the scale of the balance for at least fifteen minutes before weighing. If it is weighed immediately after being handled the flask appears 0·5 or 0·7 m.grm. too light. An error in weighing of 0·5 m.grm. causes, however, if we weigh about 2·6 grms. of soda (corresponding to the consumption of about 50 c.c. of normal acid) an error of 0·0003 in the correction figure. By "correction figure" we here signify that number of which the c.c. consumed of a standard liquid not quite correctly adjusted must be multiplied to convert them into normal acid. If, *e.g.*, there have been weighed out 2·70615 grms. Na_2CO_3, this quantity corresponds to—

$$\frac{2{\cdot}70615}{0{\cdot}05338} = 50{\cdot}696 \text{ c.c.}$$

of normal acid, *i.e.*, for its neutralisation there would be required 50·696 c.c. of an accurate normal acid.

If of the acid to be tested there were really consumed for this purpose 50·06 c.c., the correction number of this acid—

$$B - Z = \frac{50{\cdot}696}{50{\cdot}06} = 1{\cdot}0127,$$

i.e., 1000 c.c. of the tested acid for conversion into a normal acid must be made up to 1012·7 c.c., or otherwise every value read off of the acid being tested must be multiplied by this number for conversion into c.c. normal. The soda weighed out is introduced as above described into a flask of Jena apparatus glass containing about 800 c.c. mixed with 300 c.c. of hot water and a few drops of solution of litmus, and so much of the acid to be tested that the liquid appears just of an onion red. It is then heated to ebullition and kept in that condition for eight minutes. Long experience and many special experiments have shown me that at this dilution it may be boiled twice or three times as long without danger of losing even a trace of hydrochloric acid.

This is very important, since normal hydrochloric acid has so many advantages in comparison with sulphuric acid that it should be used exclusively. In addition to the advantages mentioned in Lunge's "Pocket-book for the Alkali Manufacture," it has, like the nitric acid, the highest avidity (tendency to neutralisation) of all acids, and in consequence gives with litmus a much sharper change of colour than sulphuric acid. The solution of constituents of the glass (alkali) during boiling is in case of Jena apparatus-glass so trifling that it has not the slightest influence on the result.

If we do not boil longer than from seven to eight minutes, a time fully sufficient for expelling the carbonic acid, the adjustment in case of normal acids can be effected with full satisfaction in a flask of common glass. The error committed is scarcely measurable with normal acids. Immediately after boiling, the flask, whilst being kept in constant agitation, is held in a stream of cold water, and when thus cooled it is titrated back with alkali. Any good ordinary flask will bear the sudden strong refrigeration if care is taken that the entire surface is overflowed with the cold water. A strong current of water or the total immersion of the flask in cold water is less dangerous than a partial treatment with little water. All fear of breakage is entirely obviated by the use of Jena apparatus-glass.

As long as we work with soda in normal liquids refrigeration is not absolutely necessary. The change of colour is sufficiently sharp in heat. Cooling is indispensable only for decinormal liquids and when titrating with ammonia. The reading off of the volumes of liquid consumed with burettes with fine graduation marks, which for 0·1 c.c. are 1 m.m. distant from each other, can with practice be carried to 0·02 c.c.

The use of an Erdmann float is not only quite superfluous, but on grounds which Mohr has explained it is even objectionable.

(To be continued).

People's Palace Technical Schools.—The annual meeting of the People's Palace Chemical Society will be held on Thursday, January 24, when Professor Thorpe will give an address on "Some Conditions and Causes of Chemical Change." The chair will be taken by Professor Tilden at 8 p.m. Tickets may be obtained on application to the Hon. Sec., Mr. Thomas Yetton.

A Contribution to the Knowledge of the Opium Alkaloids.—O. Hesse.—Laudanidin resembles laudanin very closely in crystalline form, solubility in various menstrua, behaviour with ferric chloride, sulphuric acid, potassa, and soda-lye. It melts in Roth's apparatus at 177° (laudanin at 166°). Codamin is isomeric with laudanin and laudanidin, and homologous with laudanosin. Laudanin probably consists of two bases, the one lævo-rotatory, and the other as strongly dextro-rotatory.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 20th, 1894.

Dr. Armstrong, President, in the Chair.

Messrs. Claude Smith and Frederick J. Allen were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Herbert Anderson, County School, Wellington, Somerset; Francis H. Carr, Meaburne, Warham Road, Croydon; Donald St. John Grant, M.A., M.B., Lahore, India; Herbert Grime, 11, Church Road, Chorlton-cum-Hardy, Manchester; John Adams Hatfield, 89, Bridge Street, Wednesbury; Percy Hudson, 48, Alexandra Road, Burton-on-Trent; Patrick Henry Kirkaldy, 68, East India Road, Poplar, E.; William Baxter McVey, 301, Saratoga Street, Boston, Mass.; Herbert Frederick Stephenson, 10, Muschamp Road, E. Dulwich, S.E.; Thomas C. Warington, 1, Charles Street, Hanley, Staffordshire; Henry Stow Young, 13, Balham Grove, S.W.

The following is the text of an address which has been sent to Professor C. Remigius Fresenius, who has now been fifty years a Foreign Member of the Society:—

"Geh. Hofrath Professor Dr. C. R. Fresenius,

"Dear Sir,

"It is little more than two years ago that the Chemical Society addressed its congratulations to Prof. Bunsen, its senior Foreign Member, on the 50th anniversary of his election into our body. It is now our privilege, on behalf of the Fellows, to address you, who come next to him on our list of Foreign Members, on a similar occasion; and to congratulate you on having so long retained your vigour and pursued your career of usefulness in that most important branch of our science, analytical chemistry, the cultivation of which you have made so especially the work of your life.

"We rejoice to have your name among those of the early contributors to our journal, communications from you on an improved method for the detection and quantitative determination of arsenic, and on inorganic constituents of plants, appearing in the second volume of our Memoirs. Indeed, you were elected into our Society at a time when it was customary to choose as Foreign Members only those chemists abroad who had become directly and intimately connected with us by contributing to our Proceedings, your name coming very early on a list of such contributors at the head of which are the names of Liebig and Bunsen.

"There are still some among us who knew you as a student; not a few also who have been students under you; but you are also well known to the Fellows generally, all of whom, indeed, feel that they owe you much gratitude for the assistance that you have afforded them, both in their studies and in their professional work, through your invaluable text-books on qualitative and quantitative analysis, and through the *Zeitschrift* you have so long conducted, which renders such signal service to chemists by keeping them informed of the progress of analytical chemistry.

"On behalf of English chemists generally, we have to express the earnest wish that you may be permitted during many years to come to continue to carry on labours which are so generally appreciated."

H. E. Armstrong, *President*.
T. E. Thorpe, *Treasurer*.
J. M. Thomson, Wyndham R. Dunstan, *Secretaries*.
R. Meldola, *Foreign Secretary*.

Of the following papers those marked * were read:—

*81. "*An Improved Form of Barometer.*" By J. Norman Collie, Ph.D.

In the improved form of barometer described by the author, several new devices are introduced. Lightness and strength are secured by using for the stem of the instrument thick Sprengel pump tubing. The upper and lower part of the barometer is made from the same piece of tubing, so that the diameter of the cisterns is the same throughout.

Just below the upper cistern a small glass trap is inserted to prevent air which may creep up the stem from entering the Torricellian vacuum. The mercury in the lower cistern is connected with the upper part of the barometer by means of a small tube of capillary bore. This capillary tube is bent just below the point of junction with the bottom of the Sprengel tube, so as to lie along the inner wall of the lower cistern; by this means an unobstructed view of the top of the mercury at the lower level is obtained.

The scale may be etched either on the barometer itself or on a thick plate-glass mirror, which is placed behind the instrument. Very accurate readings are thus obtained.

Mr. C. E. Müller has suggested a further improvement in the form of a ground-glass joint inserted in the middle of the barometer. This renders the instrument easier to fill and clean, besides allowing of its being packed in a box of convenient form.

*82. "*The Constituents of Piper Ovatum.*" By Wyndham R. Dunstan, F.R.S., and Henry Garnett.

This is a West Indian medicinal plant growing in Trinidad. When chewed it gives rise to a tingling sensation and profuse salivation, accompanied by temporary local anæsthesia. The leaves were found to contain a terpene, and a considerable quantity of physiologically active resin, which is also present in the root and stems. From this "resin" the authors were ultimately able, by a tedious process, to separate a crystalline highly active substance, which they name *piperovatine*. Its composition is expressed by the formula $C_{16}H_{21}NO_2$, and it appears to possess an alkaloidal structure, but is, nevertheless, devoid of basic properties. It is nearly insoluble in water and in dilute acid and alkalis, but dissolves readily in alcohol, and the alcoholic solution exhibits the curious property of setting to a "jelly" of very minute crystals when water is added to it.

Piperovatine acts as a temporary depressant of both motor and sensory nerves, and also as a heart poison. It produces a powerful stimulant effect on the spinal cord, causing a tonic spasm resembling that of strychnine. It seems likely to be of service in therapeutics.

*83. "*Note on the Active Constituent of the Pellitory of Medicine.*" By Wyndham R. Dunstan, F.R.S., and Henry Garnett.

The similarity in the physiological effect produced by *Piper Ovatum* and by the Pellitory of medicine (*Anacyclus pyrethrum*), led the authors to examine this plant, the activity of which is usually ascribed to a resin. The authors have separated from this resin a crystalline intensely active substance which they name *pellitorine*. In most of its chemical and physical properties it closely resembles piperovatine; but so far it has always exhibited certain small differences which may possibly disappear when the substance has been further purified. Both piperovatine and pellitorine appear to be pyridine derivatives, but neither possesses any appreciable basic power.

*84. "*The Determination of some High Temperature Freezing-points by means of Platinum-resistance Pyrometers.*" By C. T. Heycock and F. H. Neville.

From time to time the authors have communicated to the Society the results of experiments on the freezing-points of alloys in which sodium, tin, bismuth, cadmium, thallium, and lead were the solvent metals. These experiments have now been extended to temperatures above those in which a mercury thermometer could be used by means of a platinum-resistance pyrometer.

The results, recorded to the nearest whole number, are as follows:—

	Freezing-point.
Zinc	419° C.
Antimony	624 ,,
Magnesium	633 ,,
Aluminium	653 ,,
Silver	957 ,,
Copper	1081 ,,
Sodium carbonate	848 ,,
Sodium sulphate	883 ,,
Potassium sulphate	1066 ,,

In making an experiment the pyrometer is plunged into a mass of the molten substance well above its melting-point, and the falling temperature is followed until it suddenly stops. This temperature is the *freezing-point.* In the apparatus employed the temperature of freezing is maintained for a minute or more, and after this a fall is obtained which at first is very slow. If the pyrometer is now withdrawn it is found to have a very considerable quantity of solid substance adhering to it.

Discussion.

Mr. Gowland called attention to the fact that the metals experimented on were not examined for impurities, although care had been taken to procure them as nearly pure as possible from manufacturers.

Zinc as met with in commerce always contains considerable amounts of lead. In some specimens only 0·4 per cent is present, but in others as much as 1·9 per cent, and even more, is occasionally found. Zinc also contains cadmium, and this is especially the case in the so-called "pure" re-distilled metal. Whilst investigating a method for the determination of antimony in copper by the nature of the fracture of one of its alloys with zinc, he had noticed that ordinary zinc (spelter) gave satisfactory results, but when so-called "pure" zinc which had been re-distilled by the manufacturer was used, the results were altogether anomalous. On examining this zinc it was found to be contaminated with cadmium, two cakes containing 5·1 per cent, another about 3 per cent, and a fourth little more than traces.

In the case of copper, commercial samples vary much in the proportions of metallic impurities and of sub-oxide present. Even electrotype copper is sometimes impure; copper should therefore always be tested, the simplest method being a determination of its electric conductivity, as this will generally sufficiently indicate the extent of its purity. Copper when melted, even under a thick layer of charcoal, will absorb oxygen, and become contaminated with sub-oxide.

He suggested that it would be desirable in future to ascertain the chief impurities in the metals experimented on, and to determine their amounts, for even when present in small proportions they often have, as is well known, marked effects on the physical properties. This would add very greatly to the value of the determinations of their freezing-points, and would enable them to be compared with the results obtained by other observers.

*85. "*The Preparation of Adipic Acid and some of its Derivatives.*" By Walter H. Ince, Ph.D.

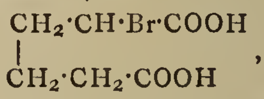
Wislicenus's method of preparing adipic acid by heating β-iodopropionic acid with silver being found to be unsatisfactory, other methods of preparation were investigated.

According to Arppe (*Zcitsch. fur Chem.*, 1865, 300), adipic acid may be readily prepared by the action of nitric acid on sebacic acid. The author finds, however, that not only has nitric acid no action on sebacic acid, but that sebacic acid crystallises unchanged from its solution in fuming nitric acid. By the action of potassium permanganate in neutral acid, and alkaline solutions, sebacic acid is entirely decomposed, yielding small quantities of a monobasic acid, but no adipic acid.

Maiaguti (*Ann. Chim. Phys.*, [3], xvi., 84) states that when beef suet is heated with ordinary nitric acid, the main product is adipic acid. The author in repeating the experiment finds that when ordinary nitric acid is used, the main product consists of sebacic and azelaïc acids, and, when fuming nitric acid is used, an acid having the formula $C_{11}H_{20}O_4$ is among the products. In neither case could the presence of adipic acid be detected.

As might be anticipated, the action of nitric acid on beef suet is a complex one, and the products vary with the concentration of the acid employed; but in no case does adipic acid appear to be formed.

a-Monobromadipic acid,—



$$\begin{array}{l}CH_2{\cdot}CH{\cdot}Br{\cdot}COOH \\ | \\ CH_2{\cdot}CH_2{\cdot}COOH\end{array},$$

was prepared by Gal and Gay-Lussac (*Annalen*, clv., 250), but was not obtained in a pure state. The author has isolated it in a state of purity by heating adipic acid (1 mol. prop.) with bromine (2 mol. props.) in a sealed tube at 160° for two hours. The semi-crystalline contents of the tube are dissolved in ether, and yield on re-crystallisation from absolute alcohol, small colourless crystals melting at 131°. When mixed with water or a dilute solution of potassium hydroxide, this acid readily changes into *a-hydroxyadipic acid*, $C_4H_7OH(COOH)_2$. This is extracted from the aqueous solution by ether, which on evaporation deposits colourless crystals melting at 151°, and subliming without decomposition. This acid is soluble in alcohol, water, and ether.

*86. "*The Action of Hydrogen Chloride on the Oxides of Calcium, Barium, and Magnesium.*" By V. H. Veley, F.R.S.

In continuation of former experiments (*Trans.*, 1893 and 1894), the author finds that dry hydrogen chloride does not act on quicklime at ordinary temperatures, or at 40°, but at 80° action occurs. Dry hydrogen chloride does not act on magnesia at ordinary temperatures; at 40°, however, action takes place to a considerable extent. Dry hydrogen chloride was observed to attack baryta at all temperatures.

Discussion.

The President expressed the opinion that our knowledge of the conditions which determine chemical change, and of the influence of water, was now such that it was necessary to adopt every possible precaution in preparing dry materials, and that the mere passage of a gas *over* a drying agent was not sufficient. He thought that on this account Mr. Veley's results were entirely inconclusive, and that the enquiry ought to have been carried further before an attempt was made to state conclusions. It was to be expected that barium oxide would be more easily acted on, as baryta was dehydrated less readily than lime or magnesia.

*87. "*Latent Heat of Fusion.*" By Holland Crompton.

If the latent heat of fusion of a unit weight of a metal is multiplied by the atomic weight of the element and divided by the absolute temperature of fusion, the resulting quantity is proportional to the valency of the metal, or in other words equivalent quantities of the metallic elements undergo on fusion equal changes in entropy. In modified form this rule is found to hold also for the non-metals.

In the case of compounds the molecular latent heat of fusion divided by the absolute temperature of fusion is also proportional to the sum of the valencies of the atoms composing the molecule. It is necessary, however, in this case to suppose that the valencies are to a certain extent influenced by the mode of union of the atoms with one another, and modified in accordance with certain definite empirical rules stated by the author.

For elements, therefore, the relationship $wA/Tv = 1{\cdot}38$, and for compounds the similar relationship $wM/T\Sigma v = 1{\cdot}38$ is found to hold: w is the latent heat of unit weight, A the atomic and M the molecular weight, T is the absolute temperature of fusion, and v and Σv are the valencies and the sum of the valencies respectively.

By combining these expressions with van 't Hoff's formular for the molecular depression of the fusing point, $E=0{\cdot}02T^2/w$, it is possible to calculate the molecular depression from the values of v and T. The numbers thus calculated are compared with those obtained by direct measurement and found to be in fair agreement. Solubilities or the melting points of mixtures of known composition can also be calculated, making use of the formula given by Schröder (*Zeit. Physikal. Chem.*, xi., 449), connecting the solubility with the latent heat of fusion and melting-point in absolute temperature. Here, again, agreement between the calculated and observed values is obtained.

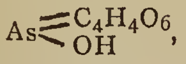
The relationship enunciated in the paper throws a new light on the question of the mechanism of the change from the solid to the liquid condition. It indicates that this change is one in which the simple chemical molecules and the atoms composing them are mainly concerned, and that it does not consist merely in the transition of complicated to simpler molecular aggregates.

88. "*Metallic Tartrarsenites.*" By G. G. Henderson, D.Sc., M.A., and A. R. Ewing, Ph.D.

Arsenious oxide dissolves readily in hot solutions of sodium hydrogen tartrate, and when the liquid is concentrated and cooled, colourless prismatic crystals of *sodium tartrarsenite*, $C_4H_4O_6AsONa{\cdot}2\frac{1}{2}H_2O$, separate. This is a stable salt, easily soluble in water, but insoluble in alcohol. The aqueous solution has an acid reaction, and when neutralised with soda gives a mixture of arsenious oxide and disodium tartrate. The corresponding *ammonium* salt resembles the sodium salt, but is more unstable, gradually decomposing, even in the solid state, into arsenious oxide and ammonium hydrogen tartrate. *Potassium tartrarsenite* is at once decomposed by cold water, and hence is prepared with greater difficulty. It is obtained as a finely crystalline precipitate. The characteristic *barium* salt, $(C_4H_4O_6AsO)_2Ba{\cdot}H_2O$, is prepared in the form of delicate lustrous needles by mixing dilute solutions of barium chloride and of the sodium salt. It is only slightly soluble in hot water, and is partially decomposed when boiled with much water, like all the salts of the series hitherto examined. The *strontium* and *calcium* salts are more soluble, and much less stable in solution. The heavy metals give precipitates with soluble tartrarsenites, but these precipitates appear to be in most cases either tartrates or mixtures of tartrates with arsenious oxide.

When the barium salt is cautiously mixed with dilute sulphuric acid, keeping the salt in excess, a clear filtrate is obtained, which has a strong acid reaction, but contains no sulphuric acid, and which gives a copious precipitate of arsenious sulphide when hydrogen sulphide is added. The solution probably contains free tartrarsenious acid, $C_4H_4O_6AsOH$, but this is too unstable to be isolated. Concentration of the solution, or raising its temperature to 60—70°, or addition of alcohol or of a trace of a mineral acid, causes decomposition of the acid into arsenious oxide and tartaric acid; but if soda is added, sodium tartrarsenite is formed, and a quantitative examination of the solution proved it to contain almost exactly the theoretical quantity of arsenic.

Experiments with other acid oxides and hydoxy-acids indicate that tartrarsenious acid is either a derivative of arsenious acid,—



$$\mathrm{As}\begin{matrix}\lessgtr C_4H_4O_6\\ \lessdot OH\end{matrix},$$

or an ethereal derivative of tartaric acid, having the formula $CO_2H{\cdot}CHO(AsO){\cdot}CHOH{\cdot}CO_2H$.

89. "*Note on the Interaction of Hydrogen Sulphide and Bismuth Haloid Compounds.*" By M. M. Pattison Muir, M.A., and Edwin M. Eagles, B.A.

The authors find that bismuth chloride and hydrogen sulphide react at a very moderate temperature, producing bismuth thiochloride, BiSCl, and hydrogen chloride; that a similar action occurs between bismuth bromide and hydrogen sulphide; but that bismuth iodide and hydrogen sulphide do not interact. They also prove that bismuth sulphide is produced by the interaction of bismuth chloride, or bromide and hydrogen sulphide at a red heat. The thiohaloid compounds, BiSCl and BiSBr, are also formed very readily by passing chlorine or bromine vapour over bismuth sulphide. Bismuth thioiodide was obtained, but not quite free from bismuth sulphide, by heating bismuth sulphide with bismuth iodide.

PHYSICAL SOCIETY.

Extra Meeting, January 11th, 1895.

Prof. A. W. Rücker, F.R.S., President, in the Chair.

This meeting was held in the physical laboratories of University College (by invitation of Professor Carey Foster).

Prof. Ramsay read a paper by himself and Miss Dorothy Marshall on "*The Measurement of Latent Heats of Vapourisation of certain Organic Liquids.*"

The liquid to be examined is placed in a small flask with a narrow neck, and within this is a platinum wire which has its two ends fused through the bottom, so as to be capable of conveying an electric current and thus giving heat to the liquid. The flask is completely enclosed in a jacket which is filled with the vapour of liquid of the same kind, kept briskly boiling in a somewhat larger flask. Before the current is turned on the vapour jacket is kept going for some time, so that the liquid in the flask is raised just to its boiling point, but no appreciable evaporation takes place. As soon as the current is turned on, boiling commences, and as the temperature of the liquid cannot be further raised, all the heat developed in the wire is expended in producing evaporation. By weighing the flask before and after, the mass of liquid vapourised is determined. So far the authors have only used the method for comparative determinations. Two arrangements of the kind described are placed side by side, and the same current is sent through their two wires, which are joined in series and have approximately equal resistances. The actual values of the resistances are found while the current is flowing, and allowance is made for their inequality. The ratio of amounts of heat expended on the two liquids divided by the ratio of the masses vapourised, is equal to the ratio of their latent heats. As a standard liquid of known latent heat, the authors prefer alcohol to water, as it vapourises more easily and with less bumping. The determinations made by this method agree well with those of other observers, but the authors' object is to obtain values correct within about ½ per cent for a large number of liquids rather than a highly accurate value for any one substance.

In reply to Mr. Griffiths, the authors stated that the platinum wire was found to rise about 20° above the temperature of the liquid, and Mr. Griffiths said that his experience had been similar. He did not see why a very high degree of accuracy should not be obtainable by the method.

Prof. Rücker expressed his admiration for the work, and thought it justified by the fact that the results accorded more nearly with theory than those of other observers.

Mr. Eumorfopoulos read a paper on "*The Determination of Thermal Conductivity and Emissivity.*"

In the first series of experiments described, two bars of the same material and polish, and each of the uniform circular section, are heated, each at one end, until the distribution of temperature has become steady. By means of two thermo-joints (one on each rod) a series of isothermal points are then found. According to the ordinary theory, if the two bars agree in temperature at a given pair of points, they will also agree in temperature at distances x_1 and x_2 measured respectively from these points, where x_1 and x_2 are connected by the relation $x_1/x_2 = \sqrt{(r_1/r_2)}$; r_1 and r_2 being the radii of the rods. This relation was not found to hold good for the rods examined, some being of brass, others of copper and of German silver. In all cases x_1/x_2 was further removed from unity than the ordinary theory would require. One conclusion was that the formula usually adopted in such cases could not be used for the comparison of conductivities, unless the radii of the rods compared are equal, and their surfaces in the same condition. For it seemed unlikely that the thermal conductivity of the smaller of each pair of rods was less than that of the thicker one. To settle the question, three brass rods were chosen, and their absolute conductivities compared by Angström's method, one end of the rod being alternately heated and cooled, and the alternations of temperature observed at two points along the rod, as soon as they had assumed a periodic character. At each point of the bar the excess of temperature over surroundings may be analysed into a Fourier's series, consisting of a constant term and series of sines and cosines. Hence both emissivity and conductivity were calculated. The emissivity was found to vary considerably with the radius, being greater the thinner the rod; moreover the value of the emissivity deduced from the first sine term of the Fourier's series was in each case found to be about 1·2 times as great as that deduced from the constant term.

Mr. A. W. Porter then read a paper "*On the Influence of the Dimensions of a Body on the Thermal Emission from its Surface.*"

The ordinary assumption is that whether a body is *in vacuo* or surrounded by air, the "emissivity" (*i.e.*, the amount of heat passing outward from unit area per second per degree excess of temperature) is independent of the size of the body. Results obtained experimentally by Péclet for cylinders and spheres of different sizes show that the emissivity depends materially upon the size of the body. Péclet's formulæ for cylinders and spheres surrounded by air show that for each of these forms the rate of emission per unit surface, exclusive of the radiation effect, may be represented by a constant *plus* a term inversely proportional to the radius. Experiments on thin wires by Messrs. Ayrton and Kilgour have also shown that the emissivity can be expressed through a considerable range of radius in the form given by Péclet, and the experiments on rods made by Mr. Eumorfopoulos and already described in this report lead to the same conclusion. The author examines the results of supposing the loss to follow only in part the law of radiation, the remainder being assumed to follow the law of conduction. He thus arrives at a formula—

$$e = h + \frac{c}{a\,(\log \mathrm{R} - \log a)},$$

where e is the emissivity, a the radius of the rod, R the radius of a hollow cylinder which surrounds the bar, and above which the excesses of temperature are reckoned, while h and c are constants. This formula has been compared with experimental results of Ayrton and Kilgour, of MacFarlane, of Bottomley, and of Péclet, and has also been directly checked by experiments on a brass rod when surrounded by water jackets of different radii, as well as on the same bar unjacketed. The author finds the agreement to be much closer than is the case on the theory of constant emissivity, or with empirically deduced formula of Ayrton and Kilgour; and he concludes that the enclosing boundary is as important a factor in determining emissivity as the size of the body itself.

Prof. Carey Foster thought that in demonstrating the influence of the enclosure Mr. Porter had established an important point.

Prof. Ayrton agreed as to the importance of the influence of the enclosure. Some years ago he had noticed that when the diameter of a wire was small, the power required to keep it red-hot by the passage of a current was nearly independent of the diameter. This would also follow from Péclet's formula. He urged that in such experiments as those of Mr. Porter and Mr. Eumorfopoulos, the conductivity and emissivity, which were functions of the temperature, should not be assumed constant along the bar.

Mr. Trotter objected to the use of the term emissivity as including loss of heat by contact with the air, in addition to the loss by radiation.

Mr. Griffiths said that in some of his experiments, where a wire conveying an electric current was immersed in a liquid in order to heat the latter, the rise of the temperature of the wire above that of the liquid was found to be nearly independent of the diameter of the wire.

Mr. Eumorfopoulos, replying to Prof. Ayrton's criticism, said that in each case his comparison had been between portions of bars in which the range of temperature was the same. Moreover, the variation of the emissivity and conductivity with temperature, as found by other observers, would be quite insufficient to account for his results.

Mr. Porter said that the term emissivity had come to be accepted as referring to all heat lost at the surface of a body, whether by radiation or by conduction and convection. In that sense he had used the term.

Prof. Rücker thought that emissivity, in this sense, was not a good term, but to change now would probably only make greater confusion.

Mr. G. U. Yule then gave a brief outline of his paper "*On the Passage of an Oscillator Wave-train through a Plate of Conducting Dielectric.*"

By a conducting dielectric the author means a substance whose conductivity and dielectric capacity are both of importance in the case under discussion, and the paper is mainly an investigation of the following problem:—A train of plane electromagnetic waves falls at normal incidence on an infinite parallel-sided plate of conducting dielectric, whose thickness is finite, and at the first face of the plate the amplitude of the vibration-vector in the incident train is zero up to a certain instant, and then becomes equal to an harmonic function of the time, multiplied by an exponential function with negative index. To find what proportion of the energy of the whole incident train is reflected back, what proportion is transmitted through the plate, and what proportion absorbed at successive incidences of reflected and re-reflected wave-trains upon the two bounding faces of the plate, the amplitudes and phase-changes of reflected and transmitted portions have to be taken into account, and the resulting infinite series of terms have to be summed. The analysis is very long, but the results obtained are exact. Curves are given showing (for special numerical values of the constants of the problem) the quasi-periodic variation of the amounts of energy transmitted and reflected, as the thickness of the plate is increased from zero up to a high value. Other curves are given showing the effect of varying the dielectric constant and the conductivity of the plate, and the difference between a "damped" and an "undamped" wave-train in regard to intensity of reflected and transmitted portions. The author compares his calculated results with measurements obtained in the case of oscillator-waves travelling along a double-wire circuit about 100 metres in length; the wires at the middle of the circuit being run through a jar containing distilled water, alcohol, or a very dilute electrolyte. The necessary corrections, however, are difficult and uncertain, and the author has not found it possible to deal with them in a satisfactory way.

A letter from Dr. E. H. Barton was read emphasizing the necessity of taking into account the damping in the oscillator-train, and at the same time pointing out why, in his opinion, the corrections applied by Mr. Yule were inadequate and failed to yield intelligible results.

Prof. Rücker congratulated Mr. Yule on his work, and on the importance of the results he had obtained.

In returning the thanks of the Society to Prof. Carey Foster for the invitation to meet in University College, he expressed the pleasure he had felt in observing the extent and completeness of the laboratories. Hitherto London had been behind the provinces in this matter, and it was gratifying to find that students in London had now such opportunities for practical instruction in physics. The papers which had been read at that meeting were a proof that good use was being made of the laboratories for the purpose of research. The educational experiments they had seen in the laboratories were excellently devised, and he hoped that many of them would become a part of the regular course of instruction in the country.

Prof. Foster briefly replied.

NOTICES OF BOOKS.

Outlines of Mathematical Chemistry. The Energetics of Chemical Phenomena. ("Grundzüge der Mathematischen Chemie. Energetik der Chemischen Erscheinungen"). By Dr. Georg Helm, Ordent Professor at the Royal Chemical High School of Dresden. With 17 Figures. Leipzig: Engelmann. 1894.

According to the author's preface, the title of this book must be understood in the same sense in which we speak of mathematical physics. He aims at collating the results of the most recent researches in the field of general chemistry according to the deductive method. Experiments are here, not as in the inductive presentation, to lead to the development of conceptions, but only to illustrate these conceptions and make the reader acquainted with their use. It would almost seem that chemistry is to lose its character as a science of observation and experiment, and in consequence to fall under the jurisdiction of a different class of minds. We cannot say that this revolution is free from a dark side. The new development will require exceptional care and judgment if it is to be truly and permanently useful to Science. It need scarcely be said that to anyone not familiar with the higher mathematics the work is utterly unintelligible.

In the successive parts Dr. Helm discusses energy, entropy, chemical intensity, and, in conclusion, the stage of multiplicity, or the freedom of chemical phenomena. Perhaps he would have done more service had he at the outset or at the conclusion presented his views free from mathematical scaffolding.

Constitution of the Aromatic Sulphones.—L. Zorn and H. Brunel.—From the existence of the paraxylene and orthoxylene sulphones, and from the fact that the sulphones of metaxylene have not been obtained, we believe we may conclude that in the aromatic sulphones the group SO_2 must be placed in the *meta*-position.—*Comptes Rendus*, cxix., No. 26.

Series of Indophenols. General Method of Preparation.—H. P. Bayrac.—The author has used a modification of the method of Kœchlin and Witt. The principle of this method consists in causing paramidodimethylaniline to react upon the phenol, not in an alkaline, but in an acetic solution. The quantity taken of the phenol which it is intended to convert into indophenol is equal to one-fifth of the molecular weight of the phenol. All these indophenols possess a number of physical characters in common. Their crystals, when measurable, belong to the triclinic system. They are almost insoluble in water, which, however, they colour a very fine blue. With ether they give a violet solution; with benzene a violet blue; with alcohol a very fine blue; with ligroine a violet red; with acetic acid a greenish blue. The mineral acids, especially if concentrated and slightly heated, destroy these compounds.—*Bulletin de la Soc. Chim. de Paris*, xi.-xii., No. 23.

CORRESPONDENCE.

THE "PROCEEDINGS OF THE CHEMICAL SOCIETY."

To the Editor of the Chemical News.

Sir,—The title-page and index of this periodical have just come to hand; and on the title-page occur the words—"Edited by the Secretaries." It is right that authors should know the precise significance of these words as lately determined by the Council of the Society.

Two courses appeared to be open:—Either to submit proofs to the authors of the abstracts of their papers sent to the Society if any substantial (*i.e.*, more than typographical) alteration had been made; in which case, the authors themselves would naturally bear the responsibility of their statements. Or, on the other hand, to throw the whole responsibility on the editors, leaving them them to make any excisions or alterations they may choose in the abstracts sent to them; or, indeed, if they so think fit, entirely to re-write them. The Council, in order to secure rapid publication, have chosen the latter alternative; and it should be understood that the abstracts are now "official," *i.e.*, the responsibility for all statements put forth rests solely on the editors of the *Proceedings*.—I am, &c.,

William Ramsay.

University College, London,
January 14, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 26, December 24, 1894.

Displacement of Carbon by Boron and Silicon in Melted Cast-iron.—Henri Moissan.—Already inserted.

L. Joué and E. Crouzel addressed to the Academy a paper on a tanno cupric liquor applicable to the treatment of mildewed vines.

Experimental Researches on Radiation at Low Temperatures.—Raoul Pictet.—The author expresses his results by means of six curves.

Contribution to the Study of Atmospheric Ozone.—J. Peyron.—The author studies the influence of vegetation on the formation of atmospheric ozone. He has made more than seven hundred observations during the months of 1894, July to October inclusive, using the iodised starch ozonoscopic paper. He concludes that vegetation favours the formation of atmospheric ozone. His papers were blackened, and he observes that the papers were least attacked if placed in conditions where oxygen is destroyed, *e.g.*, near putrescent organic matter. In the country he observed ozone every day and every night, but not in Paris except on stormy days.

On the Metallic Sulphides.—A. Villiers.—This paper will be inserted in full.

Combinations of Hexamethyleneamine with Silver Nitrate, Chloride, and Carbonate.—M. Delepine.—The author gives the percentage compositions, the formulæ, and the reactions of these compounds. He points out as remarkable the formation of compounds of silver carbonate and chloride with a base approximating to the amines.

On the Iron Chromates.—Charles Lepierre.—The author has obtained thirteen chromates, two of which only were previously known. There are double salts, and all are ferric. They are in general hydrated. All are coloured from red to yellow, passing through brown tones. The chromates derived from ferrous salts are less rich in chrome than those derived from ferric salts, and among the latter those obtained from the dichromates are the richest. The proportion of iron oxide is greatest in the chromates of the ferrous salts, and it oscillates between 23 and 26 per cent in the chromates of the ferric salts. The iron chromates form a series parallel to the basic sulphates of the same metal. They are applicable in painting on porcelain.

On the Cyanic Ethers.—Albert Colson.—Urethane is a constant product of the reaction of cyanogen chloride with ether. The author has also obtained the soluble and the insoluble cyanic ether. These two compounds are physical isomers. Both are very stable.

New Reagent for showing the Presence of Hydrogen Peroxide in Green Plants.—A. Bach.—The author places in a test-glass 5 c.c. of a solution containing 0·03 grm. potassium bichromate and 5 drops of aniline per litre. He adds 5 c.c. of the solution in question and one drop of a 5 per cent solution of oxalic acid. In presence of hydrogen peroxide there is produced a rose-violet colour. A blank experiment should be made simultaneously. Of the twenty-five plants tried, eighteen gave a positive result. Negative results were obtained with *Medicago sativa*, *Chicorium intybus*, *Avena sativa*, *Viola odorata*, and *Lilium bulbiferum*. These experiments tend to prove that the green parts of plants contain hydrogen peroxide, or peroxides which have a similar function.

On the Valence of Glucinium and the Formula of Glucina.—Alph. Combes.—According to the author's experiments, we ought, as does Mendeleeff, to consider glucinium as bivalent, having the atomic weight 9. The formula of glucina will be $Gl.O$.

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Potassium Cyanide.—The firm of Messrs. Philip Harris and Co., Limited, Birmingham, are manufacturers of potassium cyanide, 100 per cent, at a price of 3s. 9d. per pound.

Restoring Engravings.—I find a number of coloured prints, left in a book for years, have become so affected by some deleterious substance in the paper that the pigment, presumably red lead, has turned almost black with a metallic lustre. Under these circumstances I would ask if there is any acid, alkali, or other chemical with which these works might be treated so as to secure rubification and return to some of their pristine freshness?—Collector.

MEETINGS FOR THE WEEK.

Monday, 21st.—Society of Arts, 8. (Cantor Lectures). "The Arc Light," by Prof. Silvanus P. Thompson, F.R.S.
—— Medical, 8.30.
Tuesday, 22nd.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
—— Institute of Civil Engineers, 8.
—— Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Society of Arts, 4.30. "Russian Armenia and the Prospects for British Trade," by Dr. A. Markoff.
Wednesday, 23rd.—Society of Arts, 8. "Tea," by A. G. Stanton.
—— Geological, 8.
Thursday, 24th.—Royal, 4 30.
—— Institute of Electrical Engineers, 8.
—— Royal Institution, 3. "Four English Humourists of the Nineteenth Century," by W. S. Lilly, M.A.
Friday, 25th.—Royal Institution, 9. "The Nile," by Sir Colin Scott-Moncrieff, K.C.M.G.
—— Physical, 5. "On Tests of Glow Lamps," by Prof. Ayrton and Mr. Medley. "On the Temperature of Water at its Maximum Density," by Professor Anderson and Mr. McClelland.
Saturday, 19th.—Royal Institution, 3. "Stained Glass Windows and Painted Glass," by Lewis F. Day.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1835.

NATURAL GROUPS AND CROSS-ANALOGIES.

By C. T. BLANSHARD, M.A.

Natural groups of the elements are determined principally by two characters: (1) A simple connection between the atomic weights; (2) the possession of similar chemical properties. These two characters do not always suffice to group elements correctly, owing to the existence of *cross-analogies*, which will be dealt with shortly. A check on these two classifying characters is found, however, in the *dicta* of the periodic law.

Thus, the older chemists would place Cr in the same group with Mn, C in the same as B, and so on.

A list of the elements arranged in their natural groups according to the latest physical and chemical evidences, checked in this way by the periodic law, will be found in the Chem. News (lxx.. p. 271) and in the *Phil. Mag.* ([5], 39, p. 106, January, 1895), in which articles the classification of the elements is examined into from the points of view of *atomic volume*, *atomic heat*, *melting-point*, and *volume heat*.

But, for the purpose of studying various cross-analogies, I will here reproduce this classification, numbering the elements in their groups, as position in a natural group will be found to have an important bearing on the subject.

	I.	II.	III.	IV.
1.	Li	Be	B	C
2.	Na	Mg	Al	Si
3.	K	Ca	Sc	Ti
4.	Rb	Sr	Y	Zr
5.	Cs	Ba	La	Ce
6.	—	—	—	Th

	V.	VI.	VII.
1.	N	O	F
2.	P	S	Cl
3.	As	Se	Br
4.	Sb	Te	I
5.	Bi	Bo ?	—

	I.*a*.	III.*a*.
1.	Cu	Ga
2.	Ag	In
3.	Au	Tl

	V.*a*.	VI.*a*.	VII.*a*.
1.	V	Cr	Mn
2.	Nb	Mo	—
3.	Nd ?	Pr ?	—
4.	—	U	—

	II.*a*.	IV.*a*.
1.	Zn	Ge
2.	Cd	Sn
3.	Hg	Pb

	II.*b*.	IV.*b*.	VI.*b*.
1.	Fe	Co	Ni
2.	Ru	Rh	Pd
3.	Os	Ir	Pt

	I.*c*.	III.*c*.	V.*c*.	VII.*c*.
1.	Sm ?	Gd ?	—	—
2.	Dp ?	—	Ta	—

	II.*c*.	IV.*c*.	VI.*c*.
1.	—	Tb ?	Er
2.	Yb	—	W

The *c* groups here are the 10th and 11th periodic series of W. Preyer ("Das Genetische System der Chemischen Elemente," Berlin, 1893).

If we examine into these groups, either regarding the chemical or physical characters of the elements placed in them, we find that several elements might easily be considered as members of different groups than here represented; but that, looked at from the point of view of the majority of their properties, they are correctly grouped, notwithstanding.

Thus, Mendeléeff places Na as the first member of the Cu series ("Osnovoui Chimii," 1873), in which he is followed by Preyer and others; Lothar Meyer ("Moderne Theorien der Chemie," 1891) places it between Li and K. Both classifications have something to be said in their favour. Thus, J. W. Retgers (*Zeit. Phys. Chem.*, iv., 593) finds that sodium and silver nitrates are isodimorphous, viz., that from mixed solutions of the two salts, when $AgNO_3$ is in excess, rhombic crystals form; whilst, when $NaNO_3$ is in excess, hexagonal crystals take their place. Again, until a sodium-alum was produced, exactly like potassium-alums, there seemed good reason to regard Na as deviating considerably from the characters of the K series. E. Augé, however (*Comptes Rendus*, 1890, cx., 1139), by taking care to keep the solutions of the sulphates within certain limits of both t° and concentration, has succeeded in forming a definite Na alum exactly analogous to K alums.

Again, take the first elements of each group, Li, Be, B, C, N, O, and F. Mendeléeff calls these "typical elements," W. Ostwald ("Outlines of General Chemistry," Eng. trans., 1891, p. 185) shows that this name is rather unfortunate; for these elements are rather the connecting links between the various natural groups. Now, this is what we should expect on the hypothesis that the elements have a common origin. The top members of each group would have many characters in common, whereas the lower members of any one group would differ considerably, being specialised in a particular direction from the corresponding lower members of other groups. Thus, Ostwald gives as examples:—Li forms a sparingly soluble bicarbonate, like the metals of the alkaline earths, not like Na and K. Again, Be is so like Al—its oxide resembles Al_2O_3 very closely, its salts are astringent like those of Al, &c.—that, until the atomic heat of the element and the vapour-density of its chloride proved it to be allied to Mg, it was regarded as a triad. The triad Boron resembles no other element so much as it does the tetrad Carbon. The following analogies of fluorine to the first member of the hexad-group, oxygen, have been found by H. Moissan (*Bull. Soc. Chim.*, [3], v., 880):—(1) Charcoal burns in it; (2) calcium fluoride resembles the oxide rather than the chloride; (3) fluorides of metals have higher melting-points than the corresponding chlorides.

Let us take a few more examples, in order to find out the circumstances under which cross-analogies can exist between elements. Mn is isomorphous with Cr in the manganates and chromates, besides several well-known analogies of the two substances in the laboratory. These elements are the first members of two adjoining natural groups.

In the permanganates Mn is analogous to Cl—the permanganates and perchlorates being isomorphous.

Mn and Cr have nearly the same atomic weight. But not only have elements with nearly the same atomic weight cross-analogies, but also elements of nearly double (or nearly half) the atomic weights of others are analogous. Thus,—

$$Cr = 52 \text{ and } Al = \frac{54}{2}$$

are isomorphous in the alums.

A similar analogy was instanced by the writer as early as 1875 (Chem. News, xxxii., 151). Hg, with atomic weight 2×100, is analogous in its protosalts to Ag=108. This subject is being worked at by J. Traube (*Berichte*, No. 18), an account of which is given in the Chemical News (vol. lxx., p. 314).

Cu, besides being isomorphous with Ag, with which it is grouped by the periodic law, is, in certain compounds, isomorphous with Fe, Co, and Ni. These four elements have very similar atomic weights, but their atomic volumes are still closer, being nearly identical, viz., about 7. The same fact is observed in Cr and Mn, with atomic volume 7·4, and in numerous other cases of isomorphism. The connection between isomorphism and atomic volume was discovered by Schröder in 1865.

Cr has analogies with both Co and Rh (IV.*b*, 1 and 2). S. M. Jörgensen (*Journ. Prakt. Chem.*, [2], xli., 437) has investigated some complex bases containing ammonia and chlorine combined with Cr, Rh, or Co, of analogous composition.

Again, with regard to Al, P. Hautefeuille and A. Perrey (*Comptes Rendus*, cvii., 786) have found that Be can replace Al (1) in silicates of the composition—

$$6SiO_2,R_2O_3,K_2O;$$

(2) in orthoclase. Al, on the other hand, has analogies to Cr and Fe in the alums; whereas Fe as a dyad is isomorphous with dyad Zn and Mg.

In some salts Ca is isomorphous with Zn and Mg, in others with Pb, as are also Ba and Sr.

The hexad elements Mo and W are found by J. W. Retgers (*Zeit. Phys. Chem.*, viii., 6—75) to be analogous to heptad Mn by the isomorphism of K_2MoO_4, K_2WO_4, and K_2MnO_4.

W. Feit has shown ("Dissertation," Lippstadt, 1888) that Tl, though connected with the Al, Ga, and In group by its atomic weight, atomic volume, &c., has the following analogies to members of other groups:—*a*. To Pb in having nearly the same atomic volume, and in the fact that a thin layer of carbonate forms on it in the air. *b*. Thallium resembles K even more closely than it does Pb; thus (1) the carbonate is soluble in water; (2) the chloride forms double salts with $PtCl_4$; (3) its tri-iodide is like KI_3; (4) according to C. Lepierre and M. Lachaud (*Comptes Rendus*, cxiii., 196), it forms with potassium chromate the crystalline double salt $KTlCrO_4$, but not with lead chromate. To this we might add (5) the simple spectra of K and Tl, that of Pb being very complex.

Tl and Pb are the third members of groups III.*a* and IV.*a*, K being the third member of group I., and we have seen they have several analogies. In the same way the last members of groups IV. and VI.*a*, Th and U, show analogies, though to a less extent.

Thus, W. F. Hillebrand and W. H. Melville (*Amer. Chem. Journ.*, xiv., 1) find that their sulphates are isomorphous.

I think enough evidence has been cited to show that elements occupying corresponding positions in natural groups, especially in adjoining groups, offer many analogies (law of cross-analogies).

THE NOMENCLATURE OF THE PENTOSES AND PENTOSANS.

By W. E. STONE.

THERE has just come to my notice the suggestion of C. F. Cross in the CHEMICAL NEWS for December 21st as to the nomenclature of the "furfural yielding carbohydrates." It hardly seems possible that the writer is unacquainted with the terms "pentoses" and "pentosans" already in common use to designate these very bodies, although he makes no reference to them.

The furfural reaction as applied to carbohydrates is given only by the pentatomic sugars or by certain amorphous substances, which upon hydrolysis yield one or the other of these sugars. The sugars are properly named "pentoses," expressing their position in the homologous series of aldoses, including the "hexoses," "heptose," &c. All of the amorphous bodies which yield furfural in appreciable quantities under the standard conditions (distillation with dilute mineral acids) yield, when hydrolysed, in every case thus far studied, one or the other of the pentoses. The name "pentan" was applied by me to such bodies in a paper in the *American Chemical Journal*, xiii., No. 5, and also published in the *Berichte*, xxiv., p. 1657. Soon after, at the suggestion of Professor Tollens, and to avoid confusion with the term "pentane" as applied to the hydrocarbon C_5H_{12}, the name "pentosan" was first used by me in a paper in the *Journal of Analytical and Applied Chemistry*, v., No. 8. Since then the term has come into general use by writers upon this class of bodies. It expresses the relation of such bodies to the pentoses, which seems of more importance than to indicate that they both undergo a similar reaction. A use of analogous terms appears in "galactose" and "galactan" in the hexose group. The same thing also appears in the use of the specific terms "araban" and "xylan," meaning the specific pentosans which upon hydrolysis yield the pentoses "arabinose" and "xylose." These terms are all established in the literature, and are so rational that it is to be hoped they will not be superseded by such empirical expressions as "furfurose" and "furfurosans."

Purdue University, La Fayette, Indiana, U.S.A.,
January 5, 1895.

A SUBSTITUTE FOR A FUNNEL IN FILTERING LIQUIDS.

By Prof. ARTHUR M. EDWARDS, M.D.,
Late Professor of Chemistry in the Women's Medical College and College of Pharmacy, U.S.A.

ALTHOUGH out of the sphere of teaching chemistry, yet I am in the way of using chemical apparatus, being a geologist, and I still take an interest in chemistry and devise little pieces of apparatus the same as I did over forty years ago when I was assistant to my good friend Dr. John Torrey, at the College of Physicians and Surgeons of Columbia College, New York.

In washing the earths—infusorial earths, as they are called—we have to use filtered water to prevent the minute organisms present in all water from being introduced into the solutions, and thus mar the results arrived at when using the high magnifying glasses of the microscope. Distilled water will not do, for even then the little Diatomaceæ will creep in and puzzle the observer. I have used filters of various kinds, but paper filters are the most convenient. To support them a funnel of glass or similar hard material is used. To facilitate the flow a ribbed funnel has been tried, but this is inconvenient. The flow is too slow, and much of the filter is lost, being left out on account of the adherence of it to the funnel. An upward filter was tried, but that did not answer, being risky and offering a small portion to the flow. At last I did away with the funnel altogether. I now use what I think is a decided advantage. A piece of celluloid, which is collodion mixed with gum camphor, is taken and bent around in the form of a funnel, and placed in an iron retort stand ring. Into this the paper filter can be placed. The celluloid is thin, and can have holes punched in it all over so that it becomes a sieve. Most of the filter can thus be made use of, and when it is not in use the celluloid strip can be washed and put away flat like a sheet of paper.

I am sure this contrivance will be appreciated if it is only tried.

The New Gas, Argon.—At the meeting of the Royal Society on Thursday next, the 31st inst., papers will be read on the "New Gaseous Constituent of the Atmosphere," by Lord Rayleigh and Professor Ramsay, and a description of its spectrum will be given by Mr. Crookes. The reading of the papers will be followed by a discussion, in which it is expected many chemists and physicists will take part. It is our intention to publish in the next day's CHEMICAL NEWS a full report of both papers and discussion.

ON THE GUNNING METHOD FOR TOTAL NITROGEN IN FERTILISERS.

By W. E. GARRIGUES.

Compared to the Scovell-Kjeldahl nitrogen method, that of Gunning, modified to include nitrates, does not seem to have met with the favour that its cleanliness and simplicity would warrant. It is believed that this is, in the main, due to the lower results consequent upon the use of the latter process; hence the following record of an investigation of its merits.

The work was commenced by running parallel analyses on fertilisers of unknown composition, containing sodium nitrate, by both of the methods named. In each case the manipulation, adopted by the Association of Official Agricultural Chemists, was rigidly adhered to. The appended figures, being the results obtained, speak for themselves:—

Kjeldahl with zinc dust. Per cent nitrogen.	Gunning with sodium thiosulphate. Per cent nitrogen.		
3·01	2·40	2·40	
4·98	4·30	4·35	4·55
3·53	3·00	3·10	3·24
4·02	3·50	—	—
4·67	4·05	4·21	4·24

A sample was then prepared from pure sodium nitrate and tankage. The latter was valued by the plain Kjeldahl and Gunning methods and by soda-lime combustion, with the following results.—

Kjeldahl.	Gunning.	Soda-lime.
7·05	7·05	7·08

The calculated content of the mixture was 8·97 per cent nitrogen, about one-half of which was in the inorganic form. On submitting this to analysis there were obtained:—

Kjeldahl.	Gunning.
8·90	7·17
—	7·31
—	7·46

It was very evident that in the writer's hands the Gunning method, as adopted by the Association, did not convert all the nitrogen present into ammonia. After numerous and varied experiments, which, as is usual when viewed in the light of foregone events, now seem to have been largely unnecessary, successful results were finally obtained by using the same reagents, both kind and quantity, but varying the mode and order of their addition.

For convenience of reference the official directions from "Bulletin 38," U.S. Department of Agriculture, are here given:—

"In a digestion flask holding from 250 to 500 c.c. place from 0·7 to 2·8 grains of the substance to be analysed according to the amount of nitrogen present. Ten grms. of potassium sulphate, 5 grms. of sodium thiosulphate, and 30 to 35 c.c. of the salicylic acid mixture, *i.e.*, 30 c.c. of sulphuric acid to 1 grm. of salicylic acid, are then added, and the whole digested at a low temperature until frothing ceases."

The above unsatisfactory, or rather useless, results were obtained in this manner. The chief fault is in the addition of potassium sulphate at such an early stage in the process; the large quantity of dry powder forming an effectual blanket over the sample, that for some time resists the permeation of the viscid acid solution.

The best procedure was found to be:—Adding the salicylic acid mixture directly to the sample in the flask, which is then shaken until the liquid has thoroughly wetted the dry organic matter, allow to stand about fifteen minutes, and add the thiosulphate with constant shaking. This should be done in four or five portions, following with a fresh crystal only when the one previously added has completely dissolved. The potassium sulphate is then put in, and the whole again well agitated. Digest as usual.

Handled in this manner the known mixture above referred to gave:—

8·85
8·87
8·90
8·92

Another sample of dry bone tankage and sodium nitrate was prepared and passed several times through a sixty-mesh sieve. The tankage was valued as before, and showed:—

Kjeldahl.	Gunning.	Soda-lime.
4·32	4·32	4·39
4·40	4·42	—

The calculated content of the mixture was 6·49, and the analyses returned:—

Kjeldahl.	Gunning.
6·45	6·43
—	6·45
—	6·45
—	6·46

Neither method gave results sufficiently accurate for the valuation of sodium nitrate alone; a carefully prepared sample of that salt showing on analysis:—

Kjeldahl.	Gunning.
16·05	15·80
16·35	16·00
—	16·15
—	16·22
—	16·38

Theory, 16·49

It will be noticed that without a single exception the returns of analyses were below the amount actually present. No means of avoiding this loss were found. It would, therefore, seem justifiable to report the highest figure in closely agreeing duplicates instead of the customary average.

Several blanks run through to determine the freedom from nitrogen of the reagents employed gave from nil to 0·05 per cent. No corrections were made for this.

During the distillation in the Gunning process the solution frequently foams badly; so much so, that unless the flame is turned very low, the froth rises into the connecting bulb. The addition of paraffin wax does not always overcome this difficulty, and to avoid it the use of an ordinary 32 ounce wash-bottle, in place of the 500 to 600 c.c. distillation-flask, is recommended.

There is little doubt that the seat of responsibility for many minor discrepancies is imperfect preparation of the sample. Attendant upon the use of the official 25-mesh sieve, variations in the hands of the same manipulator frequently reach 0·15 per cent, even when exceptional care is exercised. It has, therefore, been found advisable in nitrated goods to quarter down the 25-mesh sample to about 2 ounces and pass that through a 60-mesh sieve; when this is done, the difference in duplicate analyses rarely exceeds 0·05 per cent, and decinormal acid and alkali often fail to show any.

Occasionally it becomes necessary to dry the sample before it can be thus finally powdered; in that case making the moisture determinations of Stillwell and Gladding ("Bul. 38," p. 19, U.S. Dept. of Agr.) is the best procedure; *i.e.*, weigh out a portion of about 10 grms. from the original package when first opened, and determine the total moisture in the water-oven, dry the remainder of the sample to dustiness, and prepare it as above; then weigh out two grms. of the fine sample simultaneously with the portion to be used for nitrogen, and ascertain the remaining moisture. A simple calculation brings the nitrogen figure back to the original condition of the goods.

Usually, however, nitrated fertilisers contain only a few per cent of moisture, as indeed they should, lest the free acid of the phosphate in the presence of water act on the easily decomposable salt and liberate nitric acid. This theoretic action has been found a sad reality by manufacturers who incorporated nitrate salts with a wet "super," the loss of plant food being accompanied by a destruction of the fibre of the bagging containing the goods.—*Journal of the American Chemical Society*, xvi., No. 12.

THE RAPID AND ACCURATE ANALYSIS OF BONE-BLACK.*

By W. D. HORNE, Ph.D.

Several years' experience in the analysis of bone-black have led me to the adoption of the following method for attaining accurate results with comparative rapidity:—

In new char, bought from the dealer, the determination of moisture is of importance, being frequently limited by contract to 3 per cent.

In char, in constant use in sugar refineries, the moisture in the revivified sample is of no importance under usual conditions.

The moisture is determined by heating 2 grms. of the unground char for two hours in a hot air-bath at 140° C. It can be weighed between watch-glasses held by a clip to prevent absorption of moisture.

A convenient way of estimating calcium carbonate is with Lunge's nitrometer, using mercury. Two grms. of the finely pulverised sample are introduced into a two-ounce Erlenmeyer flask, and moistened with 3 c.c. of a saturated solution of mercuric chloride, the tube of 10 c.c. of hydrochloric acid (sp. gr. = 1·12) introduced, and the flask closed with a rubber stopper, which, with a short glass tube and a rubber tube, is hung to the tube of the three-way cock. By tipping the acid out upon the char and properly manipulating the stop-cock, the carbon dioxide is liberated, collected, and measured. Any hydrogen sulphide given off is absorbed by the mercuric chloride. Corrections are made for temperature and atmospheric pressure.

For the determination of carbon, iron, calcium sulphate, and insoluble ash, one portion is used. In preparing the sample for analysis, the iron particles must first be removed by a magnet, and the char then ground to an almost impalpable powder.

Two grms. of this are moistened with water and treated in a four-ounce covered beaker, with 20 c.c. hydrochloric acid, and boiled gently until solution is complete, which is within thirty minutes. The beaker is filled up with boiling water, and after settling, which takes place almost immediately, decanted upon a weighed platinum Gooch crucible with asbestos plug. The carbon is washed by decantation in this way five or six times until the filtrate is free from chlorine. The original filtrate and first decanted washing contain practically all of the iron and calcium sulphate. The following wash-waters can usually be rejected. The carbon is washed out of the beaker into the Gooch, and is then washed with 80 per cent alcohol, 95 per cent alcohol and ether, each two or three times, set in a water-jacketed air-bath, and heated at 100° C. to a constant weight, which will take about three hours. The increased weight is due to carbon and ash. The carbon is burned off over the blast. The loss of weight is then carbon, and the difference is ash.

To the acid solution containing iron and calcium sulphate a drop of methyl orange solution is added and ammonia to nearly neutral reaction. Ammonium acetate is added until the solution turns yellow, and then a few drops in excess. The solution is now heated below 70° C. until complete precipitation of iron and aluminum phosphate takes place, which is usually in about twenty minutes. The precipitate, after being washed free from chlorides, is dissolved by dilute sulphuric acid into a six-ounce Erlenmeyer flask, 10 c.c. of a 10 per cent solution of sodium sulphite added, and boiled to reduce the iron and to expel the sulphur dioxide. To ascertain when this gas ceases to come over, the vapour is led from the flask through a glass tube fitting through the rubber stopper and inclining vertically downward at its outer end. Under this is held a test-tube of dilute potassium permanganate acidified with sulphuric acid. So long as sulphur dioxide issues, it will decolourise the permanganate solution in the tube when the gas is caused to bubble up through the upper half inch of the solution. When the sulphur dioxide is all out, a drop of the solution from the flask is tested with potassium sulphocyanide for ferric iron. When the reduction is complete the solution is cooled and titrated with permanganate. If alumina is to be determined, the above-mentioned precipitate of the iron and aluminum phosphates can be treated with 150 c.c. of ammonium molybdate solution to precipitate the phosphoric acid, and filtered. In the filtrate iron and alumina are precipitated as hydroxides by ammonia, filtered off, dissolved in hydrochloric acid, re-precipitated with ammonia, collected, ignited, and weighed. The two may then be separated by any of the well-known methods.

The filtrate from the iron and alumina precipitation contains the calcium sulphate. This solution is acidified with hydrochloric acid, and barium chloride added to precipitate the sulphuric acid. The barium sulphate is treated in the usual way and calculated to calcium sulphate.

Calcium sulphide may be determined by treating 5 grms. of char with 20 c.c. of nitric acid and evaporating nearly dry, adding 20 c.c. of hydrochloric acid, and evaporating again very low to expel nitric acid, taking up in hydrochloric acid, and in an aliquot portion of the filtered solution precipitating the sulphuric acid in the usual way with barium chloride. From the weight of barium sulphate found is deducted that found as above, due to calcium sulphate. The remainder is that due to calcium sulphide.

The physical condition of the char is of great importance, and should be thoroughly examined into. The grist is estimated by throwing 100 grms. upon a sieve of known mesh, shaking gently, and weighing what passes through. This portion may, in turn, be passed through successively finer sieves, and weighed after each. In shaking, the sieve should be tapped only very gently—otherwise particles of char will be forced through which correctly belong above.

To determine the density of the char it should be carefully filled into a weighed flask of 50 or 100 c.c. capacity, and of very gently sloping sides. Admitted into such a flask through a funnel, the char fills it completely without leaving vacant recesses at the shoulders. This is weighed, from which is calculated the specific gravity of the char when loose and the pounds per cubic foot. Now the flask is tapped lightly on the table, and as the char settles down more is added until no further settling takes place, and the flask is filled to the mark. This gives the weight of char when packed, from which may be calculated, as before, the specific gravity and weight per cubic foot.

As char grows old in use its porosity decreases and its specific gravity increases. It is sometimes desirable to know its porosity. To do this the weighed flask is filled with distilled water, the char introduced little by little, displacing part of the water from the flask. At the same time the water remaining displaces from the char its

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* Read before the New York Section, November 9, 1894. From the *Journal of the American Chemical Society*, xvii., No. 1, January, 1895.

contained air, which rises in minute bubbles. The flask is tapped to pack the char, and, when filled to the mark, is heated on the water-bath to expel all air. After cooling, the supernatant water is removed and the flask and contents weighed. The increased weight over that of the flask packed with char is that of the contained water, from which can be calculated the capacity of the char for any liquid of known specific gravity.

The repeated handling which bone-black receives in continued use in sugar refineries, &c., tells on it very seriously, as the friction of the grains against each other and the machinery wears it into dust. This change is slow, but in the long run is very costly, as the fine dust has to be discarded and replaced by new char.

Any method, therefore, which would enable one to judge of the relative durability of samples of char under this continued friction should be worthy of consideration. I have attempted to contrive such a test, and after a good many experiments have found one which promises well. Twenty-five grms. of the char to be tested, between sixteen and twenty-four grist, approximately, are thrown on a sieve with circular holes, one-fiftieth of an inch in diameter, the sieve shaken back and forth ten times, tapped three times, and the shaking and tapping repeated twice. This drives the dust through, and it is weighed. Dust and char are then both put into a cylinder of tinned iron four inches in diameter and two inches deep; then six glazed porcelain marbles five-sixths of an inch in diameter and weighing together 74·66 grms. are added. Now the can is shaken back and forth with slightly rotary motion 200 times, the marbles removed, and the char sifted as before. The increased weight of dust is calculated to per cent of the char used. These tests are pretty constant for different portions of the same sample of char.

The dust formed thus from a good new char was in three cases 1·72 per cent, 1·46 per cent, and 1·76 per cent. From another new char 2·68 per cent and 2·44 per cent. Two grades made by one firm gave 2·16 per cent and 2·16 per cent in one case, and 2·86 per cent and 2·87 per cent in the other. Char which had been in use ten months and whose softer parts had already been separated by use, gave 0·92 per cent and 0·94 per cent, showing that it was then in a better wearing condition than when it first entered into use.

THE PURIFICATION OF POTABLE LIQUIDS.

The distinguished French chemist M. Maumené has been experimenting on the disinfection of drinking-waters, wines, spirits, and saccharine juices. In his operations he makes use of potassium permanganate. This substance certainly burns up a number of the organic impurities present in drinking-waters, &c., and it has the decided advantage of being harmless in any quantity likely to be ingested.

M. Maumené's method is extremely simple. It consists in the use of a dilute solution of potassium permanganate (15·8 grms. to 1000 c.c. of water) in greater or smaller quantity according to the amount of impurity to be destroyed. In from fifteen to twenty minutes the solution in question, say of beet-sugar, loses its characteristic flavour and is rendered pure. Brandies and even wines may be freed in the same manner from unpleasant tastes.

At the meeting of the Chemical Society of Paris on December 5th ult., there ensued a discussion on the novelty as well as the sanitary admissibility of Prof. Maumené's process, for which a patent seems to have been obtained. It was recognised that potassium permanganate has long been in use for determining the organic impurities in waters, and no less in the purification of sewage in grossly polluted waters (in the Thames and elsewhere). But the inventor argued that the final purification of drinking-water in this manner had not been attempted.

Here, however, he seems to be mistaken. In 1873, when preparations were being made for the Ashantee war, Mr. Crookes (Chemical News, November 21, 1873) was requested by the Army Medical Department to suggest a mode of protecting our troops against the use of the highly impure waters of the Gold Coast.

After some experiments on polluted waters he recommended as an addition to the impure water the following mixture:—

Calcium permanganate..	1 part.
Aluminium sulphate	10 parts.
Fine clay	30 ,,

This mixture, in the proportion of 1 c.c. to 10,000 parts even of London sewage, effects a rapid purification.

The addition of the other ingredients along with the permanganate has the object of expediting the process and of precipitating other impurities and living organisms upon which permanganate alone has no immediate action. It was found that moving organisms survived for more than a day in an intensely red solution of permanganate. This latter fact, however, though it shows that permanganate is of little use for soldiers on the march, does not disqualify it as an addition to the reservoirs and clarifying beds of a municipal water supply.

CONTRIBUTIONS TO VOLUMETRIC ANALYSIS.*

By B. REINITZER.

(Concluded from p. 32).

The burette is held with two fingers freely suspended by its upper end against a remote background brightly illuminated, with the lowest level of the liquid at an equal height with the eye looking towards it. The closed fingers of the other unoccupied hand are moved slowly upwards close behind the burette towards the lower curved limit of the liquid until it appears to have a sharply defined black limit. We then read off. It will be perceived that this is the method of reading off described by Mohr against a background half white and half black, so modified that the graduated reading paper which he recommends is dispensed with as not suited for rapid work. By its means the parallactic error is as good as entirely avoided, and readings can be given with full certainty up to 0·02 c.c.

If in a solution to be titrated the neutral-point is found by repeatedly letting off acid and alkali, after some practice and a due observance of the above rules results may be obtained which do not vary by more than 0·02 c.c.

Differences of 0·03 c.c. in the readings effect on using 50 c.c. of acid deviations of 0·0006 in the correction number. For accurate work the temperature of the standard liquids must not be disregarded. 50 c.c. at 17°, if heated to 22°, expand to 50·05 c.c., involving an error in the correction number; or, otherwise expressed, a soda which, if titrated at 17°, shows 100 per cent, if determined with the same acid at 22°, will have apparently 100·10 per cent. As in the rooms of the manufactory the winter and summer temperatures may vary by quite 10°, an acid standardised in summer will in winter show the strength of the soda as 0·2 per cent too low.

DIAZOACETIC ESTER AND PICRIC ACID.

By EDUARD BUCHNER.

The identification of the diazo-compounds of the fatty series has gained practical interest of late in consequence of Von Pechmann's fine discovery of gaseous diazomethan. It may therefore be permissible briefly to refer to a reac-

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* *Zeitschrift Angewandte Chemie.*

tion observed some time ago, which in the case of diazoacetic ester at least renders it possible to obtain a well-crystallised derivative in a very simple manner.

If picric acid is introduced into diazoacetethylester, it passes into solution with a liberation of nitrogen. It is first refrigerated with water; after about one-half mol. has been added to one mol. of the diazo-compound, the product of the reaction is heated in a reflux condenser, and alcohol is added simultaneously, as otherwise there occurs a premature crystallisation of the new compound. Not quite a mol. of picric acid is added. The product congeals on cooling; the crystals are drained and twice re-crystallised from boiling alcohol or precipitated from alcohol by the addition of water.

There result yellowish needles, melting at 102°, which on analysis have the expected composition of trinitrophenylglycolic ethylester, and have the composition $C_{10}H_9N_3O_9$. Potassium picrate is formed from this compound by aqueous potassa-lye on prolonged contact even in the cold. Hydrazin hydrate yields, with liberation of heat, a reddish blue trinitrophenyl hydrazin, which after once re-crystallising from boiling alcohol is obtained in dark prisms of a blue metallic lustre, decomposing at 176°. Here the picric acid behaves with the diazo-compound exactly like the mineral acids; it expels the nitrogen from the diazoacetic ester exactly as it expels carbon dioxide from the carbonates.—*Berichte*, xxvii., p. 3250.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending December 31st, 1894.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, January 10th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from December 1st to December 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined, one was recorded as "clear but dull," the remainder being clear, bright, and well filtered.

The state of the river has now assumed its normal cold weather condition, and the effect of the floods of last month is imperceptible. Compared with the November figures those of December show a marked improvement in almost every particular in the Thames-derived waters. The common salt and the hardness are slightly increased consequent on the less dilution. The nitric acid is also greater, showing that the oxidation of nitrogenous matters present is effective and abundant. The oxygen required to oxidise the organic matter present is much less than before, and the organic carbon has sunk from 0·260 grain per gallon in November to 0·156. The filtration leaves little to be desired, only one sample of the 168 examined being recorded as clear but dull.

We have taken frequent samples from the different standpipes for bacteriological examination. This affords a certain guide as to the proper working of the filters. If the bacteria in any particular sample of water show signs of approaching the limit which is permissible in pure drinking water, immediate notice will be sent to the Company, so that the imperfectly filtered supply can be cut off from the distributing mains, and the defective filter remedied. The necessity for such a notice has, however, not yet arisen, as the bacteria have been very low during the month, the highest number not reaching to within 75 per cent of the permissible amount.

Special samples have also been taken from the general shafts at the different water works. The number of bacteria here have been uniformly low, the average being 30 per c.c.

The rainfall in the Thames valley has been a little above the 25-year average. The actual fall has been 2·39 inches, while the average fall is 2·10, showing an excess of 0·29 inch.

The rainfall for the year 1894 has been in excess of the average, as will be seen from the following tabular statement:—

Table Showing the Rainfall in Inches at Oxford, Month by Month, during the year 1894.

	Actual fall.	Mean of 25 years.	Deficiency.	Excess.
January	1·74	2·26	0·52	—
February	1·60	1·92	0·32	—
March	1·67	1·59	—	0·08
April	1·70	1·78	0·08	—
May	1·45	1·95	0·50	—
June	2·79	2·21	—	0·58
July	3·27	2·38	—	0·89
August	2·48	2·24	—	0·24
September.. ..	1·74	2·66	0·92	—
October	3·97	2·56	—	1·41
November.. ..	4·80	2·31	—	2·49
December.. ..	2·39	2·10	—	0·29
	29·60	25·96	2·34	5·98

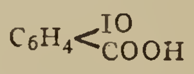
There is therefore an excess of 3·64 inches, the whole of which has fallen since the middle of October, up to which date the fall has been below the average.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

ON A NEW CLASS OF CYCLICAL IODINE COMPOUNDS OF THE IODOSO-GROUP FROM IODOPHENYLACETIC ACID.

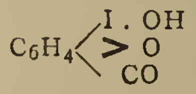
By WILHELM RAUM.

Victor Meyer and his associates have shown that the ortho-iodobenzoïc acid can easily be converted into ortho-iodosobenzoïc acid by oxidising agents. This acid, as was shown by Meyer and Wachter as early as the discovery of iodosobenzoïc acid, appears in the tautomerous forms,—



$$C_6H_4{<}{\substack{IO \\ COOH}}$$

and



$$C_6H_4{<}{\substack{I.OH \\ > O \\ CO}},$$

according to the constant tendency to the production of a pentamerous ring.

At the instigation of Prof. V. Meyer, I have investigated the behaviour of orthoiodophenylacetic acid, $I.C_6H_4.CH_2.COOH$, in which possibly the production of a ring of six members might be expected.

For comparison I have also examined the isomeric para-acid.

Production of Orthoiodophenylacetic Acid.

This acid was obtained by Mabery and Robinson. I obtained it also by dropping bromine into orthoiodotoluol heated to 200° and further elaboration of the bromide.

I used, however, a simpler method of purification than did the authors above named. 100 grms. ortho-toluol were heated to 200° on the oil-bath fitted with a reflux condenser and a dropping-funnel, and in the course of about half an hour the requisite quantity of bromine was dropped in. The product was washed, freed from uncombined iodine, and distilled along with watery vapour. At first there passed over an oil and then a crystalline mass. This was dissolved in hot ligroine, and the solution cooled in a freezing mixture, when splendid white crystals separated, melting at 54°. They are pure *orthobenzylbromide*.

This substance attacks the mucous membrane in an unbearable degree. When working with it the hands must be protected with caoutchouc gloves, as otherwise there occurs a violent eruption.

It was now converted into the nitrile by heating it for four hours in an alcoholic solution along with potassium cyanide. The nitrile is saponified with fuming hydrochloric acid, and the acid obtained is re-crystallised from much hot water. It crystallises in colourless needles melting at 106°—108°. Its composition is $C_6H_4I.CH_2.COOH$.

Mabery and Robinson give the melting-point as 95—96°. The second crystallisation of the crude acid has a more yellow colour, and melts below 100°.

Perfectly pure orthoiodophenylacetic acid, which I afterwards obtained by decomposing the iodide-chloride, melts at 110°.

For transformation into iodoso-acid, I had to use the indirect method by way of the iodide-chloride, as the direct oxidation would probably have converted the group $OH_2.COOH$ into carbonyl.

The chloride is easily obtained by introducing chlorine into the dilute solution of the acid in chloroform (3 parts of the acid in 20 of chloroform). It forms yellow crystals containing, by titration with potassium iodide, 20·9 and 20·93 per cent of active chlorine. By concentration, 21·32 per cent.

In contact with cold water the chloride loses its yellow colour. If it is ground up with water and allowed to stand for some time we obtain a white powder, which is produced in a state of purity by washing, draining on clay, drying, and extraction with ether. It melts with decomposition at 119°, and is strongly active with potassium iodide.

A volumetric determination of the iodine liberated gives 83·94 and 83·5 per cent of iodine.

This liberation of iodine would correspond to 5·29 and 5·26 per cent of active oxygen. Iodosophenylacetic acid would therefore contain theoretically 5·76 of active oxygen.

The substance contains a considerable proportion of chlorine.

The determinations of the halogens according to the method of Carius showed that the iodide-chloride gives off 1 mol. hydrochloric acid by the action of water, yielding a compound, $C_8H_6O_2ClI$.

It might, according to its composition, be regarded as a mixture of iodide-chloride and iodophenylacetic acid. But its total behaviour shows that such is not the case. It is insoluble in ether, in which the two substances named readily dissolve. A microscopic examination shows the absence of the splendidly crystalline orthophenylacetic acid, which is present to a small extent in the crude substance not yet washed with ether.

Hence a chloride has been formed which takes a mean place between an orthoiodoso-compound and an iodide-chloride. As it was expected, it contains an hexamerous ring. Representatives of this new class of substances have repeatedly been observed in this laboratory.

Experiments with Paraiodophenylacetic Acid.

From this acid I have hitherto not obtained an analogous substance.

If the iodide-chloride of the acid is boiled with water we obtain pure paraiodophenylacetic acid, as also when the iodide-chloride is dissolved in an excess of soda-lye and then acidified. On grinding up with cold water, the chloride is only very slowly attacked. Hence there does not exist an analogue of the new substance in the *para*-series, or it is formed much less readily than its isomer.

The investigation is being continued.—*Berichte*, xxvii., p. 3323.

ON THE QUALITATIVE SEPARATION OF NICKEL AND COBALT.

By A. VILLIERS.

The very distinct differences found in the action of sulphuretted hydrogen upon the salts of nickel and of cobalt may be utilised for the qualitative detection of the smallest quantities of nickel in presence of a very large excess of cobalt.

The liquid which may contain these two metals is mixed with tartaric acid and a large excess of soda (not potassa). The addition of tartaric acid is to hinder the precipitation of the metallic oxides by the alkali. It is then submitted to the action of a current of hydrogen sulphide until completely saturated (this last condition being necessary to effect the complete precipitation of the cobalt), and it is filtered immediately. In the entire absence of nickel the filtrate is quite colourless. It is only after the lapse of a considerable time that it turns yellowish by the action of the air owing to the liberation of sulphur. The presence of nickel, on the contrary, is indicated by the colouration of the filtrate, which is black if the nickel is in a considerable quantity, brown if it is less, but precipitable even if there are traces. We may thus detect the presence of nickel in a great number of commercial salts of cobalt, sold as pure. If we add a few thousandth parts of a salt of nickel to a pure salt of cobalt, the reaction is very distinct. It is therefore very sensitive, and can be applied in a few minutes.

The separation of cobalt sulphide determines a removal of a fraction of the nickel in proportions which vary with the dilution of the liquid. Inversely a certain quantity of cobalt remains in solution in a liquid containing a large excess of nickel. Thus we have not been able hitherto to utilise the above reaction for the quantitative separation of the two metals.

Salts of ammonia must not be present, and must be previously removed if necessary, as also metals precipitable by hydrogen sulphide in an acid solution or by ammonia in an acid liquid, and by ammonia in presence of ammonium chloride (after the peroxidation of the iron).

In the general case of the search for metals the filtrate from the precipitates, which may have been produced by hydrogen sulphide or by ammonia, will be precipitated by ammonium hydrosulphate prepared as recently as possible, avoiding the addition of too large an excess of the reagent. The precipitate is treated with very dilute hydrochloric acid at ebullition; the black residue, which may contain nickel and cobalt sulphides, is dissolved in a little aqua regia, and the hydrochloric solution thus obtained is submitted to the test above described after the chief part of the acid has been driven off.

A single cause of error may occur. If there is an extremely small quantity of cobalt, the precipitation of the cobalt sulphide may be hindered by the dilution, and in this case, even in the absence of nickel, we shall obtain a liquid more or less deeply coloured of a light brown. But it is sufficient to add a large excess of soda in order to obtain a complete precipitation and a filtrate perfectly colourless.

The detection of nickel may be effected still more quickly, though with less certainty, by means of the solubility of nickel sulphide in ammonium hydrosulphate, unless the latter contains sulphur in solution.

It is sufficient to pour, into a liquid mixed with ammonium hydrochlorate and ammonia, a large excess of this reagent. The presence of nickel will be shown by the brown colour of the filtrate. But under these conditions the cobalt sulphide begins to dissolve if the quantity of sulphur in solution in the ammonium hydrosulphate is very considerable. It is hence necessary to employ a reagent containing sulphur, but not too much, which would render the reaction uncertain.—*Comptes Rendus*, cxx., p. 46.

DERIVATIVES OF DIAMIDE WITH A CLOSED ATOMIC GROUPING.

By TH. CURTIUS.

TREATISE I.—*The Action of Hydrazin Hydrate on certain β and γ Ketonic Acid Esters.*

IN this first treatise the author briefly summarises former researches in this direction executed by himself, in concert with R. Jay, with K. Thum, Dr. Hans Lang, Dr. Th. Klœber, and the results of his own unpublished investigations down to the beginning of the researches of Dr. R. Von Rothenburg.

1. *Hydrazin Hydrate and Acetacetic-Acetic Ester.*—The result of the reaction is (3) methylpyrazolon, the preparation and properties of which have been already described by Curtius and Jay.

(3)-*Methylpyrazolon* forms both with acids and bases salts of little stability. (3)-Methylpyrazolon hydrochlorate is obtained by evaporating down an aqueous solution of (3)-methylpyrazolon with hydrochloric acid. In a vacuum the salt cystallises in radiating tufts. It is extremely hygroscopic.

(3)-Methylpyrazolon dissolves easily in dilute aqueous ammonia. The salt is permanent only in a dilute aqueous solution. With silver, mercury, lead, manganese, and copper salts it yields sparingly soluble precipitates.

(1)-Acetyl-(3)-methylpyrazolon is formed by the action of acetic anhydride upon (3)-methylpyrazolon, $C_6H_8N_2O_2$. It crystallises from very dilute boiling alcohol in long colourless needles melting at 140°. It is insoluble in ether and benzene, sparingly soluble in cold alcohol and ether, but more soluble on the application of heat. It is rapidly decomposed by both solvents on ebullition, acetic acid or acetic ester being split off. It behaves like a feeble acid.

(4)-*Isonitroso*-(3)-*methylpyrazolon*, $C_4H_5N_3O_2$, is obtained by passing off the red vapours (evolved from the action of nitric acid upon arsenic) into an aqueous solution of (3)-methylpyrazolon. It may also be obtained by the action of a mol. sodium nitrite upon the acetic solution of pyrazolon. It crystallises from water in yellowish silky needles, fusible at 194°, and is readily soluble in cold water and alcohol. It behaves like a powerful acid. Its aqueous solution is at once precipitated by platinum chloride, mercuric chloride, and silver nitrate. These salts have yellow to red colours.

(4)-*Isonitro*-(3)-*methylpyrazolon* silver has the composition $C_4H_4N_3O_2Ag$. It crystallises from hot glacial acetic acid in small dark red needles, which begin to decompose above 130°. If rapidly and strongly heated they detonate, giving off hydrocyanic acid.

The solution of isonitrosopyrazolon silver in glacial acetic acid is reduced by zinc powder, but (4)-amido-(3)-methylpyrazolon is not obtained.

(3)-*Methylpyrazolon*-(4)-*isonitroso ethylester*, $C_6H_9N_3O_2$, is obtained by the action of iodethyl upon the dried silver salt. The combination is explosive.

(4)-*Benzol*-(3) *methylpyrazolon* has the composition $C_6H_9N_3O_2$. (4)-Benzol-(3)-methylpyrazolon, represented by the formula $C_{10}H_{10}N_2O$, is obtained, by heating (3)-methylpyrazolon with an equi-molecular quantity of benzaldehyd. It dissolves in the liquid with a deep reddish yellow colour. It melts at 204°. It is insoluble in water, very sparingly soluble in ether or benzene.

Hydrazin Hydrate and Benzoylacetic Ester. — The reaction of these substances yields (3)-phenylpyrazolon, $C_9H_8N_2O$. It crystallises from alcohol in stout, colourless prisms, which melt at 236° with decomposition. It is almost insoluble in cold alcohol, ether, or benzene, but it is taken up to a considerable extent by boiling alcohol. With acids and bases it behaves quite like the methyl compound.

(1)-*Acetyl*-(3)-*phenylpyrazolon.*—This substance is obtained by the action of acetic anhydride in a manner quite analogous to the corresponding methyl compounds. The product after drainage by suction is rapidly re-crystallised from hot alcohol. Its composition is represented by the formula $C_{11}H_{10}N_2O_3$. It crystallises from dilute alcohol in stout, colourless prisms, fusible at 121°. It is sparingly soluble in cold alcohol and water, also in ether and benzene. The solutions are gradually decomposed with abscission of acetic acid.

The aqueous solution of the acetyl compound gives a white precipitate with silver nitrate.

(4)-*Isonitroso*-(3)-*phenylpyrazolon* is formed as a reddish precipitate on dissolving phenylpyrazolon in alcohol and introducing nitrous vapours. The precipitate on re-crystallisation from hot water forms long fine yellow needles.

(3)-*Methyl*-(4)-*pyrazolon acetic ester* is obtained at once by the action of hydrate upon acetsuccinic-ester, with the abscission of water and alcohol.

(3)-*Methyl*-(4)-*pyrazolon acetic ethylester* crystallises from alcohol in leaflets of a silvery lustre, but from water in large colourless tables which melt at 166° without decomposition. The substance is easily soluble in both liquids in heat. In benzene or ether it is sparingly soluble. If nitrous acid is introduced into the aqueous solution it gives a yellow nitroso compound.

IV.-*Hydrazin hydrate* acts upon diacetsuccinic ester very differently, according as 1 mol. or 2 mols. are caused to react with the compound. If 1 mol. diacetsuccinic ethylester is dissolved in about 10 parts of alcohol with the addition of 2 mols. hydrazin hydrate, the mixture heats spontaneously and deposits abundance of a crystalline powder sparingly soluble in almost all media. The composition of this substance is $C_4H_5N_3O$.

If 1 mol. hydrazin hydrate acts upon 1 mol. diacetsuccinic ester we have a compound of the calculated composition $C_{12}H_{18}N_2O_4$.

Levulicester and Hydrazin Hydrate.—Pure levulicethylethylester was diluted with one volume alcohol and gradually mixed with one mol. hydrazin hydrate. The reaction is quickly completed. When cold a colourless substance separates out in shining leaflets, and is purified by re-crystallisation from water. Its composition is $C_5H_{10}N_2O_2$. It may be regarded as β-acetylpropionhydrazid.

Levulichydrazid crystallises from water in large thick colourless prisms, fusible at 82°. It is moderately soluble in cold water or alcohol, less so in ether or in benzine. It is both an acid and a base. If heated above its melting point it loses a mol. of water and forms an anhydride in which an annular constitution can be recognised.

Hydrazin levulic anhydride = (3)-*methylpyridazinon* (formerly named by the author (3)-methylpyridazolon) is obtained from the hydrazid, at first obtained by heating a calculated quantity to 120° in the oil-bath. It crystallises from benzene in nacreous leaflets, fusible at 94°. It distils without decomposition at the ordinary atmospheric pressure. It appears as a homologue of (3)-methylpyrazolon.

The instability of this pyridinon ring is remarkable as compared with the striking stability of the pyrazolon ring (3)-phenylpyridazinon-(5)-carbonester.

β-*Benzoylisosuccinic acid* in an alcoholic solution was treated with gaseous hydrochloric acid with refrigeration. If the solution after standing for some time is poured into water, the ester separates out as a dark coloured oil. It was taken up with ether and shaken repeatedly, first with very dilute sulphuric acid, then with dilute soda lye, and lastly with water. The ethereal solution desiccated by calcium chloride leaves, after evaporation on the water-bath, very pure β benzoylisosuccinic ethylester as a pale yellow liquid.

Hydrazin hydrate acts upon an equi-molecular quantity of the ester thus obtained, forming (3)-phenylpyridazinon-(5)-carbonic ester. It crystallises in long colourless needles of a silky lustre, fusible at 156°, moderately soluble in cold alcohol, readily in hot alcohol and hot water, sparingly soluble in ether. It is not reduced by boiling with Fehling's solution. If heated with sulphuric acid hydrazin salt is split off.

(3)-*Phenylpyridazinon* (5)-*carbonic acid*, $C_{11}H_{10}N_2O_3$, separates from hot water as a colourless crystalline powder, fusible at 116°—117°, and is decomposed at slightly higher temperatures with abscission of carbonic acid.

(3)-*Phenylpyridazinon* (5) *carbonic hydrazid.*—This substance can be obtained from the ester above described by heating hydrazin hydrate, with the abscission of alcohol. Its composition is $C_{11}H_{12}N_4O_2$; it crystallises from hot alcohol in long splendid colourless prisms, which about 190° turn brown and are decomposed. It dissolves readily in hot water and alcohol, but is insoluble in ether and benzene. It behaves like an acidylhydrazide. On heating it reduces Fehling's solution.

Hydrazin Hydrate and β-Benzoylpropionic-ester.—These substances react with the formation of phenylpyridazon.

This substance crystallises from alcohol in stout colourless long columns, but from water in fine shining needles, fusible at 149°—150°. The crystals are sparingly soluble in cold water and ether. It has a neutral reaction, and is decomposed with difficulty on boiling with dilute sulphuric acid with the abscission of hydrazin salt. It is very stable with alkalies. It does not attack Fehling's solution even in heat.

The investigation on the action of hydrazin hydrate on the ketonic esters is being continued.

(To be continued).

THE SECRET OF THE BROWNIAN MOVEMENTS.[*]

By R. MEADE BACHE.

We first hear systematically of molecular movement, as a thing directly visible, from the writings of the distinguished botanist, Dr. Robert Brown, embodied in a paper entitled "A Brief Account of Microscopical Observations, made in the Months of June, July, and August, 1827, on the Particles contained in the Pollen of Plants; and on the General Existence of Active Molecules in Organic and Inorganic Bodies."

Of course we know inferentially, through physics and chemistry, that the particles of bodies move under the influence of various extraneous forces, and we know, too, that in the case of matter in a gaseous form they move also under the influence of force inherent in their own constitution. But the movements of which I am about to speak relate to the visible behaviour of what should be termed inert matter, if that expression were not begging the question of whether or not it has in itself power of motion, and thus deciding it in favour of the view that it has not, but is moved by extraneous force. We must begin, therefore, as is but right, by assuming that it is an open question as to whether or not certain particles, in aqueous suspension, call them molecules or otherwise, as one pleases, organic or inorganic, but not endowed with animal life, are of themselves capable of movement, or are moved by some extraneous force or forces at present unknown. The solid ground of fact from which we start is that, under the conditions mentioned, they do move, for that is undeniable and admitted.

Dr. Brown soon discarded, through disproving in the course of his investigations the surmise which he had made, that the particles of pollen indicated by their motion a mode of function analogous to that of spermatozoids, and rested eventually in the conclusion that particles moving in aqueous solutions are not confined to organic bodies or to their products. He had conducted a series of experiments on finely crushed glass, on simple earths and metals, with many of their combinations, and rocks of all ages, including those in which no organic remains have ever been found. Moving particles presented themselves in each of the constituent minerals of granite. Even a crushed fragment of the Sphynx gave the same results. He tried substances of both aqueous and igneous origin, travertine, stalactites, lava, obsidian, volcanic ashes, meteoric matter, manganese, nickel, plumbago, bismuth, antimony, arsenic, asbestos, actinolite, tremolite, zeolite, and steatite. He tried particles of wood, living and dead, linen, paper, cotton, silk, wool, hair, and muscular fibre that had been exposed to fire under the blowpipe, douched with water, and submitted to immediate examination. The particles from all these substances exhibited as vivid movement after, as before, they had been so treated.

Dr. Brown, about twelve months later, went on further to declare, under the head of "Additional Remarks on Active Molecules," that: "The result of the inquiry at present essentially agrees with that which may be collected from my printed account, and may be here briefly stated in the following terms: namely, that extremely minute particles of solid matter, whether obtained from organic or inorganic substances, when suspended in pure water, or in some other aqueous fluids, exhibit motions for which I am unable to account, and which, from their irregularity and seeming independence, resemble in a remarkable degree the less rapid motions of some of the simplest animalcules of infusions. That the smallest moving particles observed, and which I have termed active molecules, appear to be spherical, or nearly so, and to be between 1-20,000 and 1-30,000 of an inch in diameter; and that other particles of considerably greater and various size, and either of similar or of very different figure, also present analogous motions in like circumstances. I have formerly stated my belief that these motions of the particles neither arose from currents in the fluid containing them, nor depended on the intestine motion which may be supposed to accompany its evaporation. These causes of motion, however, either singly or combined with others,—as the attractions and repulsions among the particles themselves, their unstable equilibrium in the fluid in which they are suspended, their hygrometrical or capillary action, and in some cases the disengagement of volatile matter, or of minute air bubbles,—have been considered by several writers as sufficiently accounting for the appearance. Some of the alleged causes here stated, with others which I have considered it unnecessary to mention, are not likely to be overlooked or to deceive observers of any experience in microscopical research; and the insufficiency of the most important of those enumerated may, I think, be satisfactorily shown by means of a very simple experiment." (Dr. Brown here alludes to what he details at considerable length, as to the trituration together of oil and water, so as to secure, in one case, by a large proportion of water to oil, lacunæ of water of various sizes, filled with particles, protected from evaporation by the oil, and in the converse case, by a small proportion of oil to water, to secure minute oil drops on the surface of the water, some of

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[*] Read before the American Philosophical Society, April 20, 1894.—From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

which drops were not larger than the solid particles in the water).

These passages from the writings on this subject of so skillful, careful, and conscientious an observer as Dr. Brown was, excite regret that he had not pursued the subject further. He would have found, among other things, a much simpler and more lasting method of excluding air from the drop under observation, than that which he adopted in forming lacunæ of aqueous fluid protected from evaporation by immersion in oil. He would in all probability have discovered the real cause of the motion of organic and inorganic particles in aqueous fluids. But he dropped the subject, perhaps because he was obliged so to do on account of the pressure of other research, when he had obtained some valuable results, leaving his investigations negative as to conclusions. He doubtless began with the supposition, which seems common at first to all investigators of the subject, that evaporation might represent a shock that would move the particles suspended in water; that vibration from mechanical sources might account for the movements; that currents set up in the drop of water by differences of temperature in it or slight differences in the temperature of the air surrounding it, might account for them; or that mutual attractions, derived from gravitation, and inherent in the relative density of the particles themselves, might do so; and he found, as everyone else will find who experiments in these directions, that the movements go on independently of currents and independently of heat, generating or not generating currents, independently of light, and in the case where the particles represent an extremely fine division of matter, and are at the same time of low specific gravity, even independently of terrestrial gravitation; and without relation to their specific gravity, with the force of their mutual gravitation entirely masked.

Some of these things Dr. Brown implies that he saw in the course of his investigations; others he could hardly have failed incidentally to see, but one that I have mentioned he did not rightly interpret. It was a distinct lapse in his acuteness of observation, that involved in his mention, without perception of its deepest significance, of minute drops of oil, some of them not exceeding the solid particles themselves in size, standing nearly or altogether at rest on the surface of water; the pointing of which fact is very clear, one which, had it been known to me, would have induced me to try oil as well as water among the first instead of among the last of my own experiments, as actually happened in their sequence.

To afford facility for the fullest comprehension of the subject, it becomes proper here to resume the historical tenor of our way with a brief account of some of the views of Herren Wiener, Exner, and Schultze, more recent than those of Dr. Brown. In order to avoid the responsibility for the necessary condensation, I prefer to quote, as follows, from the summary of their views in the *Jahresberichte* of 1867:—

"Then Chr. Wiener, from whose account the preceding historical remarks are quoted, instituted microscopic observations of these movements, and came to the conclusion that this trembling, irregular, unsteady motion of solid molecules, which alter their direction in the briefest fraction of time in their zigzag course, has for its basis the continual movements which, by virtue of their molecular constitution, belong to fluids. He learned through his investigations (1) that the movements are not those of infusoria; (2) that the movement is not communicated to the fluid; (3) that the trembling movement is not in any way derived from the varying attraction and collision of the various oscillating molecules with one another; (4) that the movement is not derived from changes of temperature; (5) that, also, the movement is not derived from evaporation. Consequently there remained to him nothing to ascribe as the cause of the peculiar movements but the property of the fluid itself. This explanation received direct confirmation from Wiener's observation, that the amount of the movement has a certain relation to the size of the molecule. Lately S. Exner has extended the investigations of Wiener. Among the various influences which Exner sought to test with reference to the molecular motion was whether either chemical causes or mechanical ones, such as pressure, vibration, and so forth, could in any way produce an acceleration or a retardation of the effect. Only by exposure to light and heat did the motion become accelerated, and then in such a manner as, in the case of glycerin, the molecules of which under ordinary conditions show scarcely any, if any movement at all, to exhibit it clearly when warmed up to 50° C. of temperature. Exner also examined into the properties of fluids in which solid molecules remain suspended. The results of his investigation resolve themselves into the following points:—(1) The liveliness of the molecular movement is heightened by light and heat, and by radiant as well as by conducted heat; (2) one of the consequences of the molecular movement is that the molecules, in a specifically lighter fluid, not only do not sink to the bottom, but overcome the force of gravitation to such a degree as to spread themselves equally throughout the fluid; (3) the velocity of this scattering is as the intensity of the molecular movements influenced by light and heat. It should be mentioned here that Fr. Schultze had already stated that substances, when most finely divided, especially such as seemed under the microscope to be amorphous, and exhibited the brownian movements, remain suspended in pure water and in many other fluids for days, weeks, and months at a time, so that the fluid containing them presents a cloudy, or at least an opalescent appearance."

(To be continued).

PROCEEDINGS OF SOCIETIES.

UNIVERSITY COLLEGE, LONDON, CHEMICAL AND PHYSICAL SOCIETY.

January 16th, 1895.

"*On Opium.*" By Robert D. Littlefield.

The first paper of this term was given on Wednesday, January 16, and dealt with the history, cultivation, and constitution of opium gum. In the course of his remarks the lecturer referred to ancient records of opium, mentioning Scribonius Largus, A.D. 40, who gave an account of opium preparation, and Dioscorides, A.D. 70, who recorded the fact of the juice of the whole opium-bearing plant being less active than that made only from the juice of the capsule; and later Pliny, who, in addition to noting its preparation, describes its medicinal use. In ancient Latin records reference is made frequently to *Lachrima papaveris*, indicating that at that time even opium was looked upon as a most valuable drug.

Concerning the cultivation, an explanation of the formation of the latex in the plant was given, and the general manner in which the capsule was incised, the juice scraped off, and collected. The plant, as cultivated in Asia Minor, usually has white or purple flowers, and blooms in May to July according to the elevation of the land.

A naturally rich and moist soil is necessary, and a drought, frost, or locust-pest may wreck a good healthy plantation.

The opium specimens shown—kindly lent by Messrs. Hearon, Squire, and Francis—were then explained, the various characteristics being shown distinguishing the Asia Minor, Turkey, Persian, Egyptian, and Indian varieties. The peculiar narcotic bitter smell and taste were pointed out, and concerning the constitution the lecturer said that, roughly speaking, half a sample of opium consisted of albumen, fruit juice, gum, fragments of leaves, and rubbish, and the remainder contained the alkaloids, sugars, and, according to Hesse, some wax.

The acids present are sulphuric, phosphoric, and the one peculiar to the poppy, meconic. The inorganic bases are potassium, magnesium, and calcium oxides. The list of alkaloids in opium hitherto found, though very great (some 20 or so) was possibly not yet complete. Some were entirely absent from samples of the gum, and if present were only there in minute traces.

Morphine and its derivative apomorphine (discovered by Matthiesen and Wright), codein, and narcotin were the principal ones. The method of estimating the morphine in opium, as given by the British Pharmacopœia, was explained. The morphia existing in the opium as sulphate and meconate is soluble in excess of calcium hydrate.

This solution is treated with S.V.R. and ether in certain proportions, and the addition of ammonium chloride causes the precipitation of the morphia (being insoluble in the S.V.R. and ether mixture), whereas other organic substances which the NH_4Cl throws out were soluble, so that the morphia is obtained in a practically pure state, and can be weighed after the necessary drying.

After reference to apomorphine some tests for morphia were shown, and emphasis was laid on the reaction of neutral ferric chloride on an aqueous solution of opium, the beautiful red-coloured solution (that of meconate of iron) being unaffected by mercuric chloride. This being an almost conclusive test for meconic acid inferred the presence of opium in the solution tested.

In a discussion which ensued, Dr. Norman Collie referred to the ferric chloride test; he stated that some of the acetone-acetyl derivatives gave this colour exactly, and that this fact very possibly indicated the presence of this organic group in the formula of meconic acid.

Mr. Das also mentioned the effect and use of opium smoking and eating in Northern India. He remarked that there was a belief that the use of the drug was beneficial in preventing the severity of the malarial attacks and also the intensity of poisonous snake bites.

CORRESPONDENCE.

ESTIMATION OF PHOSPHORIC ACID IN THE PRESENCE OF LIME.

To the Editor of the Chemical News.

Sir,—I am not aware whether it is generally known that phosphoric acid may be estimated by the citro-magnesic method without removal of the lime.

The enormous saving of time effected by this means will be appreciated by every operator who tries this method. The results obtained are quite as accurate, in fact, I believe, more so, than when the lime is removed previous to precipitation.

The method is particularly applicable to ferruginous manures, and should then be wrought in concentrated sol.—I am, &c.,

J. G. A.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxix., No. 27, December 31, 1894.

Study of the Graphites of Iron.—Henri Moissan.—The author has proved that a great number of metals, such as aluminium, platinum, chromium, uranium, vanadium, &c., can dissolve carbon when the temperature is sufficiently high, and abandon it again in the state of graphite. On studying the conditions under which graphite is formed in one and the same metal, iron, on varying the temperature and the pressure, he has reached the following results:—1. At the ordinary pressure graphite is the purer the higher the temperature at which it is formed. 2. This graphite is so much the more stable in presence of nitric acid and potassium chlorate the higher the temperature at which it has been produced. 3. Under the influence of pressure, the crystals and the masses of graphite take the aspect of a fused matter. 4. The small quantity of hydrogen which graphites always contain decreases distinctly as their purity increases. A graphite which has not been treated with any reagent, and which has been previously heated in a vacuum, does not form water on its combustion in oxygen. 5. On attacking cast-iron with acids there are produced hydrogenous and oxygenous compounds which resist a dull-red temperature, and which, like graphite, are destroyed on combustion.

Nomination of a Correspondent for the Mineralogical Section.—M. Richthofen was elected to fill the place in this section left vacant by the decease of Kokscharow, receiving 33 votes, against 3 given to Rütimeyer, and 2 given to Tschermac.

Nickel and Cobalt Sulphides.—A. Villiers.—If we bring in contact a precipitate of nickel sulphide and ammonium sulphide there is occasioned partial solution, shown by the colour of the filtrate. The colour is very intense if the ammonium sulphide is strongly charged with sulphur. If the reagent is absolutely free from sulphur, and secured from contact of air during filtration, the totality of sulphide remains on the filter, and the filtrate is colourless. Precipitates of cobalt sulphide do not dissolve in ammonium or sodium sulphides and hydrosulphates. It is only when the latter contain a large quantity of sulphur in solution that the filtrate has a slight brown colour and contains traces of cobalt.

Calcium Ethylate.—M. de Forcrand.—The author has studied the compound which calcium carbide (CaC_2) forms with absolute ethylic alcohol. The compound is not calcium ethylate, but an addition compound of alcohol and anhydrous lime, of the composition $3CaO + 4C_2H_6O$.

On β-Oxycinchonine.—E. Jungfleisch and E. Léger.—If crystallised from strong alcohol, β-oxycinchonine forms small prismatic needles, colourless and anhydrous. It melts at 273°, but begins to be coloured at 250°. It is more dextrorotatory than α-oxycinchonine. It is almost insoluble in water, soluble in cold alcohol, but very soluble in hot alcohol. Acetone dissolves it less freely than its isomers. It dissolves also in chloroform. Its formula is $C_{28}H_{22}N_2O_4$. It is a di-acid base, and forms with monobasic acids two classes of salts: $C_{38}H_{22},N_2O_4A$ and $C_{38}H_{22}N_2O_4,2A$.

Action of Chlorine upon the Secondary Alcohols.—A. Brochet.—The action of chlorine upon the precipitated alcohols of the form $R.CHOH.CH_3$ gives acetones of the form $R.CO.CCl_3$, the radicle becoming chlorinised according to its special affinities.

Industrial Preparation and the Physiological Properties of Nicotine Oxalate and its Crystalline Salts.—H. Parenty and E. Grasset.—This paper requires the accompanying figure. It may, however, be stated that the fatal dose of pure nicotine, which is between 20 and 21 m.grms. per kilo. of the weight of the animal, rises to 70 m.grms. of combined nicotine, or 150 m.grms. of the quadroxalate per kilo. of the animal. The fatal symptoms are the same in both cases.

On the Tar of the Pine.—Adolphe Renard.—The creosote of the pine, as regards its proportion of guyacol, is intermediate between that of the beech and the oak.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., November 5, 1894.

Action of the Electric Arc upon Diamond, Amorphous Boron, and Crystalline Silicon. — Henri Moissan.—Already inserted.

Preparation and Properties of Crystalline Carbon Silicide. — Henri Moissan. — Already noticed under *Comptes Rendus.*

Preparation and Properties of Carbon Boride.—Henri Moissan.—Already noticed under *Comptes Rendus.*

Preparation in the Electric Furnace of a Crystalline Calcium Carbide. Properties of this Novel Substance.—Henri Moissan. — Noticed under *Comptes Rendus.*

Study of the Crystalline Barium and Strontium Acetylides.—Henri Moissan.

Preparation of Crystalline Aluminium Carbide.—Henri Moissan.—Carbon is capable of combining with aluminium, forming a yellow crystalline carbide of the formula C_3Al_4. This novel compound possesses well-marked reductive properties; it decomposes water slowly at common temperatures, giving off methane or formene, CH_4. This is the first instance of a similar decomposition. Perhaps this carbide has intervened in the geological phenomena which have produced for ages discharges of formene.

New Researches on Chromium.—Henri Moissan.—Already noticed under *Comptes Rendus.*

Determination of the Specific Gravity of Melted Magnesia.—Henri Moissan.—In our experiments made in the electric furnace we have always found that magnesia, purified by Schlœsing's process, cannot be reduced by coke. This fact enables us to construct the interior of our furnaces with alternate plates of magnesia and coke, and to utilise magnesia for the formation of our crucibles. The specific gravity of magnesia, after ignition in a wind-furnace for ten hours, was found to be 3·577; that of magnesia which had been exposed for two hours to the action of the arc was 3·589; and that which had been fused in the crucible of the electric furnace 3·654.

Impurities of Commercial Aluminium.— Henri Moissan.—Already inserted.

Hydrobromic Reaction of the Copper Salts.—G. Denigès.—The author maintains that the procedure given by P. Sabatier for the detection of traces of cupric salts (*Bull. Soc. Chim.*, July 20, 1894, p. 683) is substantially identical with that which he made known in 1889 (*Comptes Rendus*, cviii., p. 568; and *Soc. de Pharmacie de Bordeaux*, March and April, 1889).

Novel Series of Colouring Matters.—C. Friedel.—The author obtains a violet-red and an orange colouring matter from the product formed on heating to 120° in the oil-bath a mixture of 30 grms. methylacetanilide and 18 grms. phosphorus oxychloride until a considerable quantity of hydrochloric acid has escaped. The product dissolves in water with a yellowish brown colour. If the liquid is heated and treated with sodium carbonate, as long as effervescence is produced it takes a magenta-red and gives a precipitate of the same colour, which may be obtained by the process of "salting out."

Reduction of Nitro-aromatic Derivatives in a Neutral Liquid, and the Formation of Aromatic Hydroxyiamines.—Lumière Bros. and Seyewitz.—The process of the reduction of mononitro-aromatic derivatives in a neutral liquid by zinc-powder and water in presence of calcium chlorides enables us to obtain the corresponding hydroxylamines when there do not occur in the nucleus any hydroxylic or amidic substitutions. In the latter case we obtain the total product of reduction, amido-phenol or diamine, in a very pure state, and with a good yield.

NOTES AND QUERIES.

_ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Bronzing Copper Black.—I should be much obliged for information as to the method of bronzing copper black. It is done, I believe, by the agency of silver and copper nitrate applied to the article to be bronzed.—A. C.

MEETINGS FOR THE WEEK.

Monday, 28th.—Society of Arts, 8. (Cantor Lectures). "The Arc Light," by Prof. Silvanus P. Thompson, F.R.S.
—— Medical, 8.30.
Tuesday, 29th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
—— Institute of Civil Engineers, 8.
Wednesday, 30th.—Society of Arts, 8. "Peking," by Thos. Child.
—— British Astronomical Association, 5.
Thursday, 31st.—Royal, 4 30. "New Gaseous Constituent of the Atmosphere," by Lord Rayleigh and Prof. Ramsay, F.R.S., with Description of its Spectrum by W. Crookes, F.R.S. Discussion follows.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "Four English Humourists of the Nineteenth Century," by W. S. Lilly, M.A.
—— Society of Arts, 4.30. "India and its Women," by S. E. J. Clarke. (At Imperial Institute).
Friday, Feb. 1st.—Royal Institution, 9. "Acting—An Art," by Henry Irving.
—— Geologists' Association, 8. (Anniversary).
—— Quekett Club, 8.
Saturday, 2nd.—Royal Institution, 3. "Stained Glass Windows and Painted Glass," by Lewis F. Day.

THE CHEMICAL NEWS.

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PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

Thursday, January 31st, 1895.

The Lord Kelvin, D.C.L., LL.D., President, in the Chair.

The following papers were read:—

"*Argon: a New Constituent of the Atmosphere.*" By Lord Rayleigh, Sec. R.S., and William Ramsay, F.R.S., Professor of Chemistry, University College, London. (Abstract).

I.—*Density of Nitrogen from Various Sources.*

In a former paper[*] it has been shown that nitrogen extracted from chemical compounds is about ½ per cent lighter than "atmospheric nitrogen."

The mean numbers for the weights of gas contained in the globe used were as follows:—

From nitric oxide	2·3001
From nitrous oxide	2·2990
From ammonium nitrite	2·2987

while for "atmospheric nitrogen" there was found—

By hot copper, 1892..	2·3103
By hot iron, 1893	2·3100
By ferrous hydrate, 1894.. ..	2·3102

At the suggestion of Professor Thorpe experiments were subsequently tried with nitrogen liberated from *urea* by the action of sodium hypobromite. The hypobromite was prepared from commercial materials in the proportions recommended for the analysis of urea. The reaction was well under control, and the gas could be liberated as slowly as desired.

In the first experiment the gas was submitted to no other treatment than slow passage through potash and phosphoric anhydride, but it soon became apparent that the nitrogen was contaminated. The "inert and inodorous" gas attacked vigorously the mercury of the Töpler pump, and was described as smelling like a dead rat. As to the weight, it proved to be in excess even of the weight of atmospheric nitrogen.

The corrosion of the mercury and the evil smell were in great degree obviated by passing the gas over hot metals. For the fillings of June 6, 9, and 13 the gas passed through a short length of tube containing copper in the form of fine wire heated by a flat Bunsen burner, then through the furnace over red-hot iron, and back over copper oxide. On June 19 the furnace tubes were omitted, the gas being treated with the red-hot copper only. The mean result, reduced so as to correspond with those above quoted, is 2·2985.

Without using heat, it has not been found possible to prevent the corrosion of the mercury. Even when no urea is employed, and air, simply bubbled through the hypobromite solution, is allowed to pass with constant shaking over mercury contained in a U-tube, the surface of the metal was soon fouled.

Although the results relating to urea nitrogen are interesting for comparison with that obtained from other nitrogen compounds, the original object was not attained on account of the necessity of retaining the treatment with hot metals. We have found, however, that nitrogen from ammonium nitrite may be prepared without the employment of hot tubes whose weight agrees with that above quoted. It is true that the gas smells slightly of ammonia, easily removable by sulphuric acid, and apparently also of oxides of nitrogen. The mean result from three fillings is 2·2987.

It will be seen that, in spite of the slight nitrous smell, there is no appreciable difference in the densities of gas prepared from ammonium nitrite with and without the treatment by hot metals. The result is interesting as showing that the agreement of numbers obtained for chemical nitrogen does not depend upon the use of a red heat in the process of purification.

The five results obtained in more or less distinct ways for chemical nitrogen stand thus:—

From nitric oxide	2·3001
From nitrous oxide	2·2990
From ammonium nitrite purified at a red heat	2·2987
From urea	2·2985
From ammonium nitrite purified in the cold	2·2987
Mean..	2·2990

These numbers as well as those above quoted for "atmospheric nitrogen," are subject to a deduction of 0·0006 for the shrinkage of the globe when exhausted.[*] If they are then multiplied in the ratio of 2·3108 : 1·2572, they will express the weights of the gas in grms. per litre. Thus, as regards the mean numbers, we find as the weight per litre under standard conditions of chemical nitrogen 1·2505, that of atmospheric nitrogen being 1·2572.

It is of interest to compare the density of nitrogen obtained from chemical compounds with that of oxygen. We have $N_2 : O_2 = 2{\cdot}2984 : 2{\cdot}6276 = 0{\cdot}87471$; so that if $O_2 = 16$, $N_2 = 13{\cdot}9954$. Thus, when the comparison is with chemical nitrogen, the ratio is very nearly that of 16 : 14; but if "atmospheric nitrogen" be substituted, the ratio of small integers is widely departed from.

To the above list may be added nitrogen prepared in yet another manner, whose weight has been determined subsequently to the isolation of the new dense constituent of the atmosphere. In this case nitrogen was actually extracted from air by means of magnesium. The nitrogen thus separated was then converted into ammonia by action of water upon the magnesium nitride and afterwards liberated in the free state by means of calcium hypochlorite. The purification was conducted in the usual way, and included passage over red-hot copper and copper oxide. The following was the result:—

Globe empty, Oct. 30, Nov. 5..	2·82313
Globe full, Oct. 31	0·52395
Weight of gas.. ..	2·29918

It differs inappreciably from the mean of other results, viz., 2·2990, and is of special interest as relating to gas which at one stage of its history formed part of the atmosphere.

Another determination, with a different apparatus, of the density of "chemical" nitrogen from the same source, magnesium nitride, which had been prepared by passing "atmospheric" nitrogen over ignited magnesium, may here be recorded. The sample differed from that previously mentioned, inasmuch as it had not been subjected to treatment with red-hot copper. After treating the nitride with water, the resulting ammonia was distilled off, and collected in hydrochloric acid; the solution was evaporated by degrees, the dry ammonium chloride was dissolved in water, and its concentrated solution added to a freshly-prepared solution of sodium hypobromite.

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[*] Rayleigh, "On an Anomaly encountered in Determinations of the Density of Nitrogen Gas," *Roy. Soc. Proc.*, vol. lv., p. 340, 1894.

[*] Rayleigh, "On the Densities of the Principal Gases," *Roy. Soc. Proc.*, vol. liii., p. 134, 1893.

The nitrogen was collected in a gas-holder over water which had previously been boiled, so as, at all events partially, to expel air. The nitrogen passed into the vacuous globe through a solution of potassium hydroxide, and through two drying-tubes, one containing soda-lime, and the other phosphoric anhydride.

At 18·38° C. and 754·4 m.m. pressure, 162·843 c.c. of this nitrogen weighed 0·18963 grm. Hence,

Weight of 1 litre at 0° C. and 760 m.m. pressure = 1·2521 grm.

The mean result of the weight of 1 litre of "chemical" nitrogen has been found to equal 1·2505. It is therefore seen that "chemical" nitrogen, derived from "atmospheric" nitrogen, without any exposure to red-hot copper, possesses the usual density.

Experiments were also made, which had for their object to prove that the ammonia produced from the magnesium nitride is identical with ordinary ammonia, and contains no other compound of a basic character. For this purpose the ammonia was converted into ammonium chloride, and the percentage of chlorine determined by titration with a solution of silver nitrate which had been standardised by titrating a specimen of pure sublimed ammonium chloride. The silver solution was of such a strength that 1 c.c. precipitated the chlorine from 0·001701 grm. of ammonium chloride.

1. Ammonium chloride from orange-coloured sample of magnesium nitride contained 66·35 per cent of chlorine.

2. Ammonium chloride from blackish magnesium nitride contained 66·35 per cent of chlorine.

3. Ammonium chloride from nitride containing a large amount of unattacked magnesium contained 66·30 per cent of chlorine.

Taking for the atomic weights of hydrogen H = 1·0032, of nitrogen N = 14·04, and of chlorine Cl = 35·46, the theoretical amount of chlorine in ammonium chloride is 66·27 per cent.

From these results—that nitrogen prepared from magnesium nitride, obtained by passing "atmospheric" nitrogen over red-hot magnesium, has the density of "chemical" nitrogen, and that ammonium chloride, prepared from magnesium nitride, contains practically the same percentage of chlorine as pure ammonium chloride —it may be concluded that red-hot magnesium withdraws from "atmospheric nitrogen" no substance other than nitrogen capable of forming a basic compound with hydrogen.

II.—*Reasons for Suspecting a Hitherto Undiscovered Constituent in Air.*

When the discrepancy of weights was first encountered, attempts were naturally made to explain it by contamination with known impurities. Of these the most likely appeared to be hydrogen, present in the lighter gas in spite of the passage over red-hot cupric oxide. But inasmuch as the intentional introduction of hydrogen into the heavier gas, afterwards treated in the same way with cupric oxide, had no effect upon its weight, this explanation had to be abandoned, and finally it became clear that the difference could not be accounted for by the presence of any known impurity. At this stage it seemed not improbable that the lightness of the gas extracted from chemical compounds was to be explained by partial dissociation of nitrogen molecules N_2 into detached atoms. In order to test this suggestion both kinds of gas were submitted to the action of the silent electric discharge, with the result that both retained their weights unaltered. This was discouraging, and a further experiment pointed still more markedly in the negative direction. The chemical behaviour of nitrogen is such as to suggest that dissociated atoms would possess a high degree of activity, and that even though they might be formed in the first instance, their life would probably be short. On standing they might be expected to disappear, in partial analogy with the known behaviour of ozone. With this idea in view, a sample of chemically prepared nitrogen was stored for eight months. But at the end of this time the density showed no sign of increase, remaining exactly as at first.*

Regarding it as established that one or other of the gases must be a mixture, containing, as the case might be, an ingredient much heavier or much lighter than ordinary nitrogen, we had to consider the relative probabilities of the various possible interpretations. Except upon the already discredited hypothesis of dissociation, it was difficult to see how the gas of chemical origin could be a mixture. To suppose this would be to admit two kinds of nitric acid, hardly reconcilable with the work of Stas and others upon the atomic weight of that substance. The simplest explanation in many respects was to admit the existence of a second ingredient in air from which oxygen, moisture, and carbonic anhydride had already been removed. The proportional amount required was not great. If the density of the supposed gas were double that of nitrogen, one-half per cent only by volume would be needed; or if the density were but half as much again as that of nitrogen, then 1 per cent would still suffice. But in accepting this explanation, even provisionally, we had to face the improbability that a gas surrounding us on all sides, and present in enormous quantities, could have remained so long unsuspected.

The method of most universal application by which to test whether a gas is pure or a mixture of components of different densities is that of diffusion. By this means Graham succeeded in effecting a partial separation of the nitrogen and oxygen of the air, in spite of the comparatively small difference of densities. If the atmosphere contain an unknown gas of anything like the density supposed, it should be possible to prove the fact by operations conducted upon air which had undergone atmolysis. This experiment, although in view from the first, was not executed until a later stage of the inquiry (§ 6), when results were obtained sufficient of themselves to prove that the atmosphere contains a previously unknown gas.

But although the method of diffusion was capable of deciding the main, or at any rate the first question, it held out no prospect of isolating the new constituent of the atmosphere, and we therefore turned our attention in the first instance to the consideration of methods more strictly chemical. And here the question forced itself upon us as to what really was the evidence in favour of the prevalent doctrine that the inert residue from air after withdrawal of oxygen, water, and carbonic anhydride, is all of one kind.

The identification of "phlogisticated air" with the constituent of nitric acid is due to Cavendish, whose method consisted in operating with electric sparks upon a short column of gas confined with potash over mercury at the upper end of an inverted U-tube.†

Attempts to repeat Cavendish's experiment in Cavendish's manner have only increased the admiration with which we regard this wonderful investigation. Working on almost microscopical quantities of material, and by operations extending over days and weeks, he thus established one of the most important facts in chemistry. And what is still more to the purpose, he raises as distinctly as we could do, and to a certain extent resolves, the question above suggested. The passage is so important that it will be desirable to quote it at full length.

"As far as the experiments hitherto published extend, we scarcely know more of the phlogisticated part of our atmosphere than that it is not diminished by lime-water, caustic alkalis, or nitrous air; that it is unfit to support fire or maintain life in animals; and that its specific gravity is not much less than that of common air: so that though the nitrous acid, by being united to phlogiston, is converted into air possessed of these properties,

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* *Roy. Soc. Proc.*, lv., p. 344, 1894.

† "Experiments on Air," *Phil. Trans*, lxxv., p. 372, 1785.

and consequently, though it was reasonable to suppose that part at least of the phlogisticated air of the atmosphere consists of this acid united to phlogiston, yet it was fairly to be doubted whether the whole is of this kind, or whether there are not in reality many different substances compounded together by us under the name of phlogisticated air. I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to nitrous acid, or whether there was not a part of a different nature to the rest, which would refuse to undergo that change. The foregoing experiments indeed in some measure decided this point, as much the greatest part of the air let up into the tube lost its elasticity; yet as some remained unabsorbed it did not appear for certain whether that was of the same nature as the rest or not. For this purpose I diminished a similar mixture of dephlogisticated and common air, in the same manner as before, till it was reduced to a small part of its original bulk. I then, in order to decompound as much as I could of the phlogisticated air which remained in the tube, added some dephlogisticated air to it, and continued the spark until no further diminution took place. Having by these means condensed as much as I could of the phlogisticated air, I let up some solution of liver of sulphur to absorb the dephlogisticated air; after which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the phlogisticated air let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$th part of the whole."

Although Cavendish was satisfied with his result, and does not decide whether the small residue was genuine, our experiments about to be related render it not improbable that his residue was really of a different kind from the main bulk of the "phlogisticated air," and contained the gas now called argon.

Cavendish gives data* from which it is possible to determine the rate of absorption of the mixed gases in his experiment. This was about 1 c.c. per hour, of which two-fifths would be nitrogen.

III.—*Methods of Causing Free Nitrogen to Combine.*

To eliminate nitrogen from air, in order to ascertain whether any other gas could be detected, involves the use of some absorbent. The elements which have been found to combine directly with nitrogen are: boron, silicon, titanium, lithium, strontium, barium, magnesium, aluminium, mercury, and, under the influence of an electric discharge, hydrogen in presence of acid, and oxygen in presence of alkali. Besides these, a mixture of barium carbonate and carbon at a high temperature is known to be effective. Of those tried, magnesium in the form of turnings was found to be the best. When nitrogen is passed over magnesium, heated in a tube of hard glass to bright redness, combustion with incandescence begins at the end of the tube through which the gas is introduced, and proceeds regularly until all the metal has been converted into nitride. Between 7 and 8 litres of nitrogen can be absorbed in a single tube; the nitride formed is a porous, dirty orange-coloured substance.

IV.—*Early Experiments on Sparking Nitrogen with Oxygen in Presence of Alkali.*

In our earliest attempts to isolate the suspected gas by the method of Cavendish, we used a Ruhmkorff coil of medium size actuated by a battery of five Grove cells. The gases were contained in a test-tube standing over a large quantity of weak alkali, and the current was conveyed in wires insulated by U-shaped glass tubes passing through the liquid round the mouth of the test-tube. With the given battery and coil a somewhat short spark or arc of about 5 m.m. was found to be more favourable than a longer one. When the mixed gases were in the right proportion the rate of absorption was about 30 c.c. per hour, or thirty times as fast as Cavendish could work with the electrical machine of his day.

To take an example, one experiment of this kind started with 50 c.c. of air. To this oxygen was gradually added until, oxygen being in excess, there was no perceptible contraction during an hour's sparking. The remaining gas was then transferred at the pneumatic trough to a small measuring vessel, sealed by mercury, in which the volume was found to be 1·0 c.c. On treatment with alkaline pyrogallate the gas shrank to 0·32 c.c. That this small residue could not be nitrogen was argued from the fact that it had withstood the prolonged action of the spark, although mixed with oxygen in nearly the most favourable proportion.

The residue was then transferred to the test-tube with an addition of another 50 c.c. of air, and the whole worked up with oxygen as before. The residue was now 2·2 c.c., and, after removal of oxygen, 0·76 c.c.

Although it seemed almost impossible that these residues could be either nitrogen or hydrogen, some anxiety was not unnatural, seeing that the final sparking took place under somewhat abnormal conditions. The space was very restricted, and the temperature (and with it the proportion of aqueous vapour) was unduly high. But any doubts that were felt upon this score were removed by comparison experiments in which the whole quantity of air operated on was very small. Thus, when a mixture of 5 c.c. of air with 7 c.c. of oxygen was sparked for 1¼ hours, the residue was 0·47 c.c., and after removal of oxygen 0·06 c.c. Several repetitions having given similar results, it became clear that the final residue did not depend upon anything that might happen when sparks passed through a greatly reduced volume, *but was in proportion to the amount of air operated upon.*

No satisfactory examination of the residue which refused to be oxidised could be made without the accumulation of a larger quantity. This, however, was difficult of attainment at the time in question. It was thought that the cause probably lay in the solubility of the gas in water, a suspicion since confirmed. At length, however, a sufficiency was collected to allow of sparking in a specially constructed tube, when a comparison with the air spectrum, taken under similar conditions, proved that, at any rate, the gas was not nitrogen. At first scarcely a trace of the principal nitrogen lines could be seen, but after standing over water for an hour or two these lines became apparent.

V.—*Early Experiments on Withdrawal of Nitrogen from Air by means of Red-hot Magnesium.*

A preliminary experiment carried out by Mr. Percy Williams on the absorption of atmospheric nitrogen, freed from oxygen by means of red-hot copper, in which the gas was not passed over, but simply allowed to remain in contact with the metal, gave a residue of density 14·88. This result, although not conclusive, was encouraging; and an attempt was made, on a larger scale, by passing atmospheric nitrogen backwards and forwards over red-hot magnesium from one large gas-holder to another to obtain a considerable quantity of the heavier gas. In the course of ten days about 1500 c.c. were collected and transferred gradually to a mercury gas-holder, from which the gas was passed over soda-lime, phosphoric anhydride, magnesium at a red heat, copper oxide, soda-lime, and phosphoric anhydride into a second mercury gas-holder. After some days the gas was reduced in volume to about 200 c.c., and its density was found to be 16·1. After further absorption, in which the volume was still further reduced, the density of the residue was increased to 19·09.

On passing sparks for several hours through a mixture of a small quantity of this gas with oxygen, its volume was still further reduced. Assuming that this reduction

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* *Phil. Trans.*, lxxviii., p. 271, 1788.

was due to the further elimination of nitrogen, the density of the remaining gas was calculated to be 20·0.

The spectrum of the gas of density 19·09, though showing nitrogen bands, showed many other lines which were not recognisable as belonging to any known element.

VI.—*Proof of the Presence of Argon in Air by means of Atmolysis.*

It has already (§ 2) been suggested that if "atmospheric nitrogen" contains two gases of different densities, it should be possible to obtain direct evidence of the fact by the method of atmolysis. The present section contains an account of carefully conducted experiments directed to this end.

The atmolyser was prepared (after Graham) by combining a number of "churchwarden" tobacco pipes. At first twelve pipes were used in three groups, each group including four pipes connected in series. The three groups were then connected in parallel, and placed in a large glass tube closed in such a way that a partial vacuum could be maintained in the space outside the pipes by a water pump. One end of the combination of pipes was open to the atmosphere; the other end was connected to a bottle aspirator, initially full of water, and so arranged as to draw about 2 per cent of the air which entered the other end of the pipes. The gas collected was thus a very small proportion of that which leaked through the pores of the pipes, and should be relatively rich in the heavier constituents of the atmosphere. The flow of water from the aspirator could not be maintained very constant, but the rate of 2 per cent was never much exceeded.

The air thus obtained was treated exactly as ordinary air had been treated in determinations of the density of atmospheric nitrogen. Oxygen was removed by red-hot copper, followed by cupric oxide, ammonia by sulphuric acid, moisture and carbonic acid by potash and phosphoric anhydride.

In a total weight of approximately 2·3 grms. the excess of weight of the diffused nitrogen over ordinary atmospheric nitrogen was in four experiments, 0·0049, 0·0014, 0·0027, 0·0015.

The mean excess of the four determinations is 0·00262 grm., or, if we omit the first, which depended upon a vacuum weighing of two months old, 0·00187 grm.

The gas from prepared air was thus in every case denser than from unprepared air, and to an extent much beyond the possible errors of experiment. The excess was, however, less than had been expected, and it was thought that the arrangement of the pipes could be improved. The final delivery of gas from each of the groups in parallel being so small in comparison with the whole streams concerned, it seemed possible that each group was not contributing its proper share, and even that there might be a flow in the wrong direction at the delivery end of one or two of them. To meet this objection, the arrangement in parallel had to be abandoned, and for the remaining experiments eight pipes were connected in simple series. The porous surface in operation was thus reduced, but this was partly compensated for by an improved vacuum. Two experiments were made under the new conditions, in which the excess was I., 0·0037; II., 0·0033.

The excess being larger than before is doubtless due to the greater efficiency of the atmolysing apparatus. It should be mentioned that the above recorded experiments include all that have been tried, and the conclusion seems inevitable that "atmospheric nitrogen" is a mixture, and not a simple body.

It was hoped that the concentration of the heavier constituent would be sufficient to facilitate its preparation in a pure state by the use of prepared air in substitution for ordinary air in the oxygen apparatus. The advance of 3½ m.m. on the 11 m.m., by which atmospheric nitrogen is heavier than chemical nitrogen, is indeed not to be despised, and the use of prepared air would be convenient if the diffusion apparatus could be set up on a large scale and be made thoroughly self-acting.

VII.—*Negative Experiments to prove that Argon is not derived from Nitrogen from Chemical Sources.*

Although the evidence of the existence of argon in the atmosphere, derived from the comparison of densities of atmospheric and chemical nitrogen and from the diffusion experiments (§ VI.), appeared overwhelming, we have thought it undesirable to shrink from any labour that would tend to complete the verification. With this object in view, an experiment was undertaken and carried to a conclusion on November 13, in which 3 litres of chemical nitrogen, prepared from ammonium nitrite, were treated with oxygen in precisely the manner in which atmospheric nitrogen had been found to yield a residue of argon. The gas remaining at the close of the large scale operation was worked up as usual with battery and coil until the spectrum showed only slight traces of the nitrogen lines. When cold, the residue measured 4 c.c. This was transferred, and after treatment with alkaline pyrogallate to remove oxygen measured 3·3 c.c. If atmospheric nitrogen had been employed, the final residue should have been about 30 c.c. Of the 3·3 c.c. actually left, a part is accounted for by an accident, and the result of the experiment is to show that argon is not formed by sparking a mixture of oxygen and chemical nitrogen.

In a second experiment of the same kind 5660 c.c. of nitrogen from ammonium nitrite was treated with oxygen. The final residue was 3·5 c.c. and was found to consist mainly of argon.

The source of the residual argon is to be sought in the water used for the manipulation of the large quantities of gas (6 litres of nitrogen and 11 litres of oxygen) employed. When carbonic acid was collected in a similar manner and subsequently absorbed by potash, it was found to have acquired a contamination consistent with this explanation.

Negative experiments were also carried out, absorbing nitrogen by means of magnesium. In one instance 3 litres of nitrogen prepared from ammonium chloride and bleaching-powder was reduced in volume to 4·5 c.c., and on sparking with oxygen its volume was further reduced to about 3 c.c. The residue appeared to consist of argon. Another experiment, in which 15 litres of nitrogen from ammonium nitrite was absorbed, gave a final residue of 3·5 c.c. Atmospheric nitrogen, in the latter case, would have yielded 150 c.c., hence less than $\frac{1}{40}$th of the normal quantity was obtained. It should be mentioned that leakage occurred at one stage, by which perhaps 200 c.c. of air entered the apparatus; and, besides, the nitrogen was collected over water from which it doubtless acquired some argon. Quantitative negative experiments of this nature are exceedingly difficult, and require a long time to carry them to a successful conclusion.

VIII.—*Separation of Argon on a Large Scale.*

To prepare argon on a large scale, air is freed from oxygen by means of red-hot copper. The residue is then passed from a gas-holder through a combustion tube, heated in a furnace, and containing copper, in order to remove all traces of oxygen; the issuing gas is then dried by passage over soda-lime and phosphorus pentoxide, after passage through a small U-tube containing sulphuric acid, to indicate the rate of flow. It then enters a combustion-tube packed tightly with magnesium turnings, and heated to redness in a second furnace. From this tube it passes through a second index-tube, and enters a small gas-holder capable of containing 3 or 4 litres. A single tube of magnesium will absorb from 7 to 8 litres of nitrogen. The temperature must be nearly that of the fusion of the glass, and the current of gas must be carefully regulated, else the heat developed by the union of the magnesium with nitrogen will fuse the tube.

Having collected the residue from 100 or 150 litres of atmospheric nitrogen, which may amount to 4 or 5 litres, it is transferred to a small gas-holder connected with an apparatus, whereby, by means of a species of a self-acting Sprengel's pump, the gas is caused to circulate through a tube half filled with copper and half with copper oxide; it then traverses a tube half filled with soda-lime and half with phosphorus pentoxide; it then passes a reservoir of about 300 c.c. capacity, from which, by raising a mercury reservoir, it can be expelled into a small gas-holder. Next it passes through a tube containing magnesium turnings heated to bright redness. The gas is thus freed from any possible contamination with oxygen, hydrogen, or hydrocarbons, and nitrogen is gradually absorbed. As the amount of gas in the tubes and reservoir diminishes in volume, it draws supplies from the gas-holder, and, finally, the circulating system is full of argon in a pure state. The circulating system of tubes is connected with a mercury pump, so that, in changing the magnesium tube, no gas may be lost. Before ceasing to heat the magnesium tube the system is pumped empty, and the collected gas is restored to the gas-holder; finally, all the argon is transferred from the mercury reservoir to the second small gas-holder, which should preferably be filled with water saturated with argon, so as to prevent contamination from oxygen or nitrogen; or, if preferred, a mercury gas-holder may be employed. The complete removal of nitrogen from argon is very slow towards the end, but circulation for a couple of days usually effects it.

The principal objection to the oxygen method of isolating argon, as hitherto described, is the extreme slowness of the operation. In extending the scale we had the great advantage of the advice of Mr. Crookes, who not long since called attention to the flame rising from platinum terminals, which convey a high tension alternating electric discharge, and pointed out its dependence upon combustion of the nitrogen and oxygen of the air.* The plant consists of a De Meritens alternator, actuated by a gas engine, and the currents are transformed to a high potential by means of a Ruhmkorff or other suitable induction coil. The highest rate of absorption of the mixed gases yet attained is 3 litres per hour, about 3000 times that of Cavendish. It is necessary to keep the apparatus cool, and from this and other causes a good many difficulties have been encountered.

In one experiment of this kind, the total air led in after seven days' working, amounted to 7925 c.c., and of oxygen (prepared from chlorate of potash), 9137 c.c. On the eighth and ninth days oxygen alone was added, of which about 500 c.c. was consumed, while there remained about 700 c.c. in the flask. Hence the proportion in which the air and oxygen combined was as 79 : 96. The progress of the removal of the nitrogen was examined from time to time with the spectroscope, and became ultimately very slow. At last the yellow line disappeared, the contraction having apparently stopped for two hours. It is worthy of notice that with the removal of the nitrogen, the arc discharge changes greatly in appearance, becoming narrower and blue rather than greenish in colour.

The final treatment of the residual 700 c.c. of gas was on the model of the small scale operations already described. Oxygen or hydrogen could be supplied at pleasure from an electrolytic apparatus, but in no way could the volume be reduced below 65 c.c. This residue refused oxidation, and showed no trace of the yellow line of nitrogen, even under favourable conditions.

When the gas stood for some days over water, the nitrogen line reasserted itself in the spectrum, and many hour's sparking with a little oxygen was required again to get rid of it. Intentional additions of air to gas free from nitrogen showed that about 1½ per cent was clearly, and about 3 per cent was conspicuously, visible. About the same numbers apply to the visibility of nitrogen in oxygen when sparked under these conditions, that is, at atmospheric pressure, and with a jar connected to the secondary terminals.

IX.—*Density of Argon prepared by means of Oxygen.*

A first estimate of the density of argon prepared by the oxygen method was founded upon the data already recorded respecting the volume present in air, on the assumption that the accurately known densities of atmospheric and of chemical nitrogen differ on account of the presence of argon in the former, and that during the treatment with oxygen nothing is oxidised except nitrogen. Thus, if—

D = density of chemical nitrogen,
D' = ,, atmospheric nitrogen,
d = ,, argon,
α = proportional volume of argon in atmospheric nitrogen,

the law of mixtures give—

$$\alpha d + (1-\alpha)D = D',$$

or—

$$d = D + (D'-D)/\alpha.$$

In this formula $D'-D$ and α are both small, but they are known with fair accuracy. From the data already given—

$$\alpha = \frac{65}{0{\cdot}79 \times 7925},$$

whence if (on an arbitrary scale of reckoning) $D = 2{\cdot}2990$, $D' = 2{\cdot}3102$, we find $d = 3{\cdot}378$. Thus if N_2 be 14, or O_2 be 16, the density of argon is 20·6.

A direct determination by weighing is desirable, but hitherto it has not been feasible to collect by this means sufficient to fill the large globe employed for other gases. A *mixture* of about 400 c.c. of argon with pure oxygen, however, gave the weight 2·7315, 0·1045 in excess of the weight of oxygen, viz., 2·6270. Thus, if α be the ratio of the volume of argon to the whole volume, the number for argon will be—

$$2{\cdot}6270 + 0{\cdot}1045/\alpha.$$

The value of α, being involved only in the excess of weight above that of oxygen, does not require to be known very accurately. Sufficiently concordant analyses by two methods gave $\alpha = 0{\cdot}1845$; whence for the weight of the gas we get 3·193, so that, if $O_2 = 16$, the density of the gas would be 19·45. An allowance for residual nitrogen, still visible in the gas before admixture of oxygen, raises this number to 19·7, which may be taken as the density of pure argon resulting from this determination.

X.—*Density of Argon prepared by means of Magnesium.*

The density of the original sample of argon prepared has already been mentioned. It was 19·09; and, after sparking with oxygen, it was calculated to be 20·0. The most reliable results of a number of determinations give it as 19·90. The difficulty in accurately determining the density is to make sure that all nitrogen has been removed. The sample of density 19·90 showed no spectrum of nitrogen when examined in a vacuum tube. It is right, however, to remark that the highest density registered was 20·38. But there is some reason here to distrust the weighing of the vacuous globe.

XI.—*Spectrum of Argon.*

The spectrum of argon, seen in a vacuum tube of about 3 m.m. pressure, consists of a great number of lines, distributed over almost the whole visible field. Two lines are specially characteristic; they are less refrangible than the red lines of hydrogen or lithium, and serve well to identify the gas, when examined in this way. Mr. Crookes, who will give a full account of the spectrum in a separate communication, has kindly furnished us with the accurate wave-lengths of these lines, as well as of some others next to be described; they are respectively 696·56 and 705·64, 10^{-6} m.m.

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* Chemical News, lxv., p. 301, 1892.

Besides these red lines, a bright yellow line, more refrangible than the sodium line, occurs at 603·84. A group of five bright green lines occurs next, besides a number of less intensity. Of the group of five, the second, which is perhaps the most brilliant, has the wave-length 561·00. There is next a blue or blue violet line of wavelength 470·2; and last, in the less easily visible part of the spectrum, there are five strong violet lines, of which the fourth, which is the most brilliant, has the wavelength 420·0.

Unfortunately, the red lines, which are not to be mistaken for those of any other substance, are not easily seen when a jar discharge is passed through argon at atmospheric pressure. The spectrum seen under these conditions has been examined by Professor Schuster. The most characteristic lines are perhaps those in the neighbourhood of F, and are very easily seen if there be not too much nitrogen, in spite of the presence of some oxygen and water vapour. The approximate wave-lengths are—

487·91..	Strong.
[486·07]	F.
484·71..	Not quite so strong.
480·52..	Strong.
476·50..	Fairly strong characteristic triplet.
473·53..	
472·56..	

It is necessary to anticipate Mr. Crookes's communication, and to state that when the current is passed from the induction coil in one direction, that end of the capillary tube next the positive pole appears of a redder, and that next the negative pole of a bluer hue. There are, in effect, two spectra, which Mr. Crookes has succeeded in separating to a considerable extent. Mr. E. C. Baly,* who has noticed a similar phenomenon, attributes it to the presence of two gases. He says:—"When an electric current is passed through a mixture of two gases, one is separated from the other and appears in the negative glow." The conclusion would follow that what we have termed "argon" is in reality a mixture of two gases which have as yet not been separated. This conclusion, if true, is of great importance, and experiments are now in progress to test it by the use of other physical methods. The full bearing of this possibility will appear later.

The presence of a small quantity of nitrogen interferes greatly with the argon spectrum. But we have found that in a tube with platinum electrodes, after the discharge has been passed for four hours, the spectrum of nitrogen disappears, and the argon spectrum manifests itself in full purity. A specially constructed tube with magnesium electrodes, which we hoped would yield good results, removed all traces of nitrogen, it is true; but hydrogen was evolved from the magnesium, and showed its characteristic lines very strongly. However, these are easily identified. The gas evolved on heating magnesium *in vacuo*, as proved by a separate experiment, consists entirely of hydrogen.

Mr. Crookes has proved the identity of the chief lines of the spectrum of gas separated from air-nitrogen by aid of magnesium with that remaining after sparking the air-nitrogen with oxygen in presence of caustic soda solution. Professor Schuster has also found the principal lines identical in the spectra of the two gases, as observed by the jar discharge at atmospheric pressure.

XII.—*Solubility of Argon in Water.*

Determinations of the solubility in water of argon prepared by sparking, gave 3·94 volumes per 100 of water at 12°. The solubility of gas prepared by means of magnesium was found to be 4·05 volumes per 100 at 13·9°. The gas is therefore about 2½ times as soluble as nitrogen, and possesses approximately the same solubility as oxygen.

The fact that argon is more soluble than nitrogen would lead us to expect it in increased proportion in the dissolved gases of rain-water. Experiment has confirmed this anticipation. "Nitrogen" prepared from the dissolved gases of water supplied from a rain-water cistern was weighed upon two occasions. The weights, corresponding to those recorded in § I., were 2·3221 and 2·3227, showing an excess of 24 m.grms. above the weight of true nitrogen. Since the corresponding excess for "atmospheric nitrogen" is 11 m.grms. we conclude that the water "nitrogen" is relatively more than twice as rich in argon.

On the other hand, gas evolved from the hot spring at Bath, and collected for us by Dr. A. Richardson, gave a residue after removal of oxygen and carbonic acid, whose weight was only about midway between that of true and atmospheric nitrogen.

XIII.—*Behaviour at Low Temperatures.**

Preliminary experiments, carried out to liquefy argon at a pressure of about 100 atmospheres, and at a temperature of −90°, failed. No appearance of liquefaction could be observed.

Professor Charles Olszewski, of Cracow, the well-known authority on the constants of liquefied gases at low temperatures, kindly offered to make experiments on the liquefaction of argon. His results are embodied in a separate communication, but it is allowable to state here that the gas has a lower critical point and a lower boiling point than oxygen, and that he has succeeded in solidifying argon to white crystals. The sample of gas he experimented with was exceptionally pure, and had been prepared by help of magnesium. It showed no trace of nitrogen when examined in a vacuum tube.

XIV.—*Ratio of Specific Heats.*

In order to decide regarding the elementary or compound nature of argon, experiments were made on the velocity of sound in it. It will be remembered that, from the velocity of sound in a gas, the ratio of specific heat at constant pressure to that at constant volume can be deduced by means of the equation—

$$n\lambda = v = \sqrt{\left\{\frac{e}{d}(1+\alpha t)\frac{C_p}{C_v}\right\}},$$

when n is the frequency, λ the wave-length of sound, v its velocity, e the isothermal elasticity, d the density, $(1+\alpha t)$ the temperature correction, C_p the specific heat at constant pressure, and C_v that at constant volume. In comparing two gases at the same temperature, each of which obeys Boyle's law with sufficient approximation, and in using the same sound, many of these terms disappear, and the ratio of specific heats of one gas may be deduced from that of the other, if known, by means of the proportion—

$$\lambda^2 d : \lambda'^2 d' :: 1{\cdot}41 : x,$$

where, for example, λ and d refer to air, of which the ratio is 1·41, according to observations by Röntgen, Wüllner, Kayser, and Jamin and Richard.

Two completely different series of observations, one in a tube of about 2 m.m. diameter, and one in one of 8 m.m., made with entirely different samples of gas, gave, the first, 1·65 as the ratio, and, the second, 1·61.

Experiments made with the first tube, to test the accuracy of its working, gave for carbon dioxide the ratio 1·276, instead of 1·288, the mean of all previous determinations; and the half wave-length of sound in hydrogen was found to be 73·6, instead of 74·5, the mean of those previously found. The ratio of the specific heats of hydrogen found was 1·39, instead of 1·402.

There can be no doubt, therefore, that argon gives practically the ratio of specific heats, viz., 1·66 proper to a gas in which all the energy is translational. The only

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* Proc. Phys. Soc., 1893, p. 147.

* The arrangements for the experiments upon this branch of the subject were left entirely in Professor Ramsay's hands.

other gas which has been found to behave similarly is mercury gas, at a high temperature.*

XV.—*Attempts to induce Chemical Combination.*

Many attempts to induce argon to combine will be described in full in the complete paper. Suffice it to say here that all such attempts have as yet proved abortive. Argon does not combine with oxygen in presence of alkali under the influence of the electric discharge, nor with hydrogen in presence of acid or alkali also when sparked; nor with chlorine, dry or moist, when sparked; nor with phosphorus at a bright-red heat; nor with sulphur at bright redness. Tellurium may be distilled in a current of the gas; so may sodium and potassium, their metallic lustre remaining unchanged. It is unabsorbed by passing it over fused red-hot caustic soda, or soda-lime heated to bright redness; it passes unaffected over fused and bright red-hot potassium nitrate; and red-hot sodium peroxide does not combine with it. Persulphides of sodium and calcium are also without action at a red-heat. Platinum-black does not absorb it, nor does platinum sponge, and wet oxidising and chlorinating agents, such as nitro-hydrochloric acid, bromine water, bromine and alkali, and hydrochloric acid and potassium permanganate, are entirely without action. Experiments with fluorine are in contemplation, but the difficulty is great; and an attempt will be made to produce a carbon arc in the gas. Mixtures of sodium and silica and of sodium and boracic anhydride are also without action; hence it appears to resist attack by nascent silicon and by nascent boron.

XVI.—*General Conclusions.*

It remains, finally, to discuss the probable nature of the gas, or mixture of gases, which we have succeeded in separating from atmospheric air, and which we provisionally name *argon*.

The presence of argon in the atmosphere is proved by many lines of evidence. The high density of "atmospheric nitrogen," the lower density of nitrogen from chemical sources, and the uniformity in the density of samples of chemical nitrogen prepared from different compounds, lead to the conclusion that the cause of the anomaly is the presence of a heavy gas in air. If that gas possess the density 20 compared with hydrogen, "atmospheric" nitrogen should contain of it approximately 1 per cent. This is, in fact, found to be the case, Moreover, as nitrogen is removed from air by means of red-hot magnesium, the density of the remaining gas rises proportionately to the concentration of the heavier constituent.

Second.—This gas has been concentrated in the atmosphere by diffusion. It is true that it has not been freed from oxygen and nitrogen by diffusion, but the process of diffusion increases, relatively to nitrogen, the amount of argon in that portion which does not pass through the porous walls. This has been proved by its increase in density.

Third.—As the solubility of argon in water is relatively high, it is to be expected that the density of the mixture of argon and nitrogen, pumped out of water along with oxygen, should, after the removal of the oxygen, be higher than that of "atmospheric" nitrogen. Experiment has shown that the density is considerably increased.

Fourth.—It is in the highest degree improbable that two processes, so different from each other, should manufacture the same product. The explanation is simple if it be granted that these processes merely eliminate nitrogen from an "atmospheric" mixture. Moreover, as argon is an element, or a mixture of elements, its manufacture would mean its separation from one of the substances employed. The gas which can be removed from red-hot magnesium in a vacuum has been found to be wholly hydrogen. Nitrogen from chemical sources has been practically all absorbed by magnesium, and also when sparked in presence of oxygen; hence argon cannot have resulted from the decomposition of nitrogen. That it is not produced from oxygen is sufficiently borne out by its preparation by means of magnesium.

Other arguments could be adduced, but the above are sufficient to justify the conclusion that argon is present in the atmosphere.

The identity of the leading lines in the spectrum, the similar solubility and the similar density, appear to prove the identity of the argon prepared by both processes.

Argon is an element, or a mixture of elements, for Clausius has shown that if K be the energy of translatory motion of the molecules of a gas, and H their whole kinetic energy, then—

$$\frac{K}{H} = \frac{3(C_p - C_v)}{2C_v}$$

C_p and C_v denoting as usual the specific heat at constant pressure and at constant volume respectively. Hence if, as for mercury vapour and for argon (§ XIV.), the ratio of specific heats $C_p : C_v$ be $1\frac{2}{3}$, it follows that $K = H$, or that the whole kinetic energy of the gas is accounted for by the translatory motion of its molecules. In the case of mercury the absence of interatomic energy is regarded as proof of the monatomic character of the vapour, and the conclusion holds equally good for argon.

The only alternative is to suppose that if argon molecules are di- or polyatomic, the atoms acquire no relative motion, even of rotation, a conclusion exceedingly improbable in itself and one postulating the sphericity of such complex groups of atoms.

Now a monatomic gas can be only an element, or a mixture of elements; and hence it follows that argon is not of a compound nature.

From Avogadro's law, the density of a gas is half its molecular weight; and as the density of argon is approximately 20, hence its molecular weight must be 40. But its molecule is identical with its atom; hence its atomic weight, or, if it be a mixture, the mean of the atomic weights of that mixture, taken for the proportion in which they are present, must be 40.

There is evidence both for and against the hypothesis that argon is a mixture: for, owing to Mr. Crookes's observations of the dual character of its spectrum; against, because of Professor Olszewski's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; and because on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well-known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture. The conclusions which follow are, however, so startling that in our future experimental work we shall endeavour to decide the question by other means.

For the present, however, the balance of evidence seems to point to simplicity. We have therefore to discuss the relations to other elements of an element of atomic weight 40. We inclined for long to the view that argon was possibly one or more than one of the elements which might be expected to follow fluorine in the periodic classification of the elements—elements which should have an atomic weight between 19, that of fluorine, and 23, that of sodium. But this view is completely put out of court by the discovery of the monatomic nature of its molecules.

The series of elements possessing atomic weights near 40 are—

Chlorine	35·5
Potassium	39·1
Calcium	40·0
Scandium	44·0

There can be no doubt that potassium, calcium, and

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* Kundt and Warburg, *Pog. Ann.*, cxxxv., pp. 337 and 527

scandium follow legitimately their predecessors in the vertical columns, lithium, beryllium, and boron, and that they are in almost certain relation with rubidium, strontium, and (but not so certainly) yttrium. If argon be a single element, then there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which cannot be fitted among those of which it is composed. On the other hand, if argon be a mixture of two elements, they might find place in the eighth group, one after chlorine and one after bromine. Assuming 37 (the approximate mean between the atomic weights of chlorine and potassium) to be the atomic weight of the lighter element, and 40 the mean atomic weight found, and supposing that the second element has an atomic weight between those of bromine, 80, and rubidium, 85·5, viz., 82, the mixture should consist of 93·3 per cent of the lighter, and 6·7 per cent of the heavier element. But it appears improbable that such a high percentage as 6·7 of a heavier element should have escaped detection during liquefaction.

If it be supposed that argon belongs to the eighth group, then its properties would fit fairly well with what might be anticipated. For the series, which contains—

$$\mathrm{Si}_n^{\mathrm{IV.}},\ \mathrm{P}_4^{\mathrm{III.\ and\ V.}},\ \mathrm{S}_{8\ \mathrm{to}\ 2}^{\mathrm{II.\ to\ VI.}},\ \text{and}\ \mathrm{Cl}_2^{\mathrm{I.\ to\ VII.}},$$

might be expected to end with an element of monatomic molecules of no valency, *i.e.*, incapable of forming a compound, or if forming one, being an octad; and it would form a possible transition to potassium, with its monovalence, on the other hand. Such conceptions are, however, of a speculative nature; yet they may be perhaps excused, if they in any way lead to experiments which tend to throw more light on the anomalies of this curious element.

In conclusion, it need excite no astonishment that argon is so indifferent to reagents. For mercury, although a monatomic element, forms compounds which are by no means stable at a high temperature in the gaseous state; and attempts to produce compounds of argon may be likened to attempts to cause combination between mercury gas at 800° and other elements. As for the physical condition of argon, that of a gas, we possess no knowledge why carbon, with its low atomic weight, should be a solid, while nitrogen is a gas, except in so far as we ascribe molecular complexity to the former and comparative molecular simplicity to the latter. Argon, with its comparatively low density and its molecular simplicity, might well be expected to rank among the gases. And its inertness, which has suggested its name, sufficiently explains why it has not previously been discovered as a constituent of compound bodies.

We would suggest for this element, assuming provisionally that it is not a mixture, the symbol A.

We have to record our thanks to Messrs. Gordon, Kellas, and Matthews, who have materially assisted us in the prosecution of this research.

Mr. Crookes (before reading his paper) said—Allow me, Mr. President, to take this opportunity of striking the key-note of the chorus of applause and congratulations which will follow from all chemists present on this most valuable and important paper. The difficulties in a research of this kind are peculiar. Here we have a new chemical element, the principal properties of which seem to be the negation of all chemical properties. Chemists will understand how difficult it is to deal with anything which forms no compounds and unites with nothing. The discovery commenced by a prediction, followed after an interval by realisation. Discoveries of this kind are more important and take a higher rank, than discoveries which more or less come in a haphazard sort of way. The prediction and discovery of argon are only equalled by the few discoveries of elements which have been made in chemistry by the careful study of the periodic law, and to surpass it we must go back to the predicted existence and subsequent discovery of an unknown planet by Adams and Leverrier.

"*On the Spectra of Argon.*" By William Crookes, F.R.S., &c. (Abstract).

Through the kindness of Lord Rayleigh and Professor Ramsay I have been enabled to examine the spectrum of this gas in a very accurate spectroscope, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train.

Argon resembles nitrogen in that it gives two distinct spectra, according to the strength of the induction current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, the argon spectra both consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not at first show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord Rayleigh, Professor Ramsay, and myself, and however free it was supposed to be from nitrogen, I could always detect the nitrogen bands in its spectrum. These, however, soon disappear when the induction spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum tubes best adapted for showing the spectra are of the ordinary Plücker form, having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is 3 m.m. At this point the colour of the discharge is an orange-red, and the spectrum is rich in red rays, two being especially prominent at wavelengths 696·56 and 705·64. On passing the current the traces of nitrogen bands soon disappear, and the argon spectrum is seen in a state of purity. At this pressure the platinum from the poles spatters over the glass of the bulbs owing to what I have called "electrical evaporation,"* and I think the residual nitrogen is absorbed by the finely-divided metal. Similar absorptions are frequently noticed by those who work much with vacuum tubes.

If the pressure is further reduced, and a Leyden jar intercalated in the circuit, the colour of the luminous discharge changes from red to a rich steel blue, and the spectrum shows an almost entirely different set of lines. It is not easy to obtain the blue colour and spectrum entirely free from the red. The red is easily got by using a large coil† actuated with a current of 3 ampères and 6 volts. There is then no tendency for it to turn blue.

The blue colour may be obtained with the large coil by actuating it with a current of 3·84 ampères and 11 volts, intercalating a jar of 50 square inches surface. The make-and-break must be screwed up so as to vibrate as rapidly as possible. The red glow is produced by the positive spark, and the blue by the negative spark.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen.‡ In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow 80 lines, making 199 lines in all; of these, 26 appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the tube for some time when platinum terminals are sealed in. This is not the only way of purifying the argon. By the kindness of Professor Ramsay I was allowed to take some vacuum tubes to his laboratory and there exhaust and fill them with some of his purest argon. On this occasion I simultaneously filled, exhausted, and sealed off two Plücker tubes, one having platinum and the other aluminium terminals. On testing the gas immediately after they were sealed off, each tube showed the argon spectrum, contaminated by a trace of nitrogen

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* *Roy. Soc. Proc.*, vol. l, p. 88, June, 1891.

† The coil used has about sixty miles of secondary wire, and when fully charged gives a torrent of sparks 24 inches long. The smaller coil gives six-inch sparks when worked with six half-pint Grove cells.

‡ Photographs of the different spectra of argon, and other gaseous spectra for comparison, were projected on the screen.

bands. The next day the tube with platinum terminals was unchanged, but that having aluminium terminals showed the pure spectrum of argon, the faint nitrogen bands having entirely disappeared during the night. After an hour's sparking and a few days' rest the tube with platinum terminals likewise gave a pure argon spectrum. When a mixture of argon with a very little nitrogen is sparked in a tube made of pure fused quartz, without inside metallic terminals, the nitrogen bands do not disappear from the argon spectrum, but the spectra of argon and nitrogen continue to be seen simultaneously.

A vacuum tube was filled with pure argon and kept on the pump while observations were made on the spectrum of the gas as exhaustion proceeded. The large coil was used with a current of 8·84 ampères and 11 volts; no jar was interposed. At a pressure of 3 m.m. the spectrum was that of the pure red glow. This persisted as the exhaustion rose, until at a pressure of about half a m.m. flashes of blue light made their appearance. At a quarter of a m.m. the colour of the ignited gas was pure blue, and the spectrum showed no trace of the red glow.

An experiment was now made to see if the small quantity of argon normally present in the atmosphere could be detected without previous concentration. Nitrogen was prepared from the atmosphere by burning phosphorus, and was purified in the usual manner. This gas, well dried over phosphoric anhydride, was passed into a vacuum tube, the air washed out by two fillings and exhaustions, and the tube was finally sealed off at a pressure of 52 m.m. It was used for photographing the band spectrum of nitrogen on several occasions, and altogether it was exposed to the induction current from the large coil for eight hours before any change was noticed. The last time when photographing its spectrum difficulty was experienced in getting the spark to pass, so I increased the current and intercalated a small jar. The colour immediately changed from the reddish yellow of nitrogen to the blue of argon, and on applying the spectroscope the lines of argon shone out with scarcely any admixture of nitrogen bands. With great difficulty and by employing a very small jar I was able to take one photograph of its spectrum and compare it with the spectrum of argon from Professor Ramsay, both being taken on the same plate, but the tube soon became non-conducting, and I could not then force a spark through, except by employing a dangerously large current. Whenever a flash passed it was of a deep blue colour. Assuming that the atmosphere contains 1 per cent of argon, the 3 m.m. of nitrogen originally in the tube would contain 0·03 m.m. of argon. After the nitrogen had been absorbed by the spattered platinum, this pressure of argon would be near the point of non-conduction.

In all cases when argon has been obtained in this manner the spectrum has been that of the blue-glowing gas. Very little of the red rays can be seen. The change from red to blue is chiefly dependent on the strength and heat of the spark: partly also on the degree of exhaustion. It is not improbable, and I understand that independent observations have already led the discoverers to the same conclusion—that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum. The theory that it is a simple body has, however, support from the analogy of other gases. Thus, nitrogen has two distinct spectra, one or the other being produced by varying the pressure and intensity of the spark. I have made vacuum tubes containing rarefied nitrogen which show either the fluted band or the sharp line spectrum by simply turning the screw of the make-and-break: exactly as the two spectra of argon can be changed from one to the other.

I have prepared tubes containing other gases as well as nitrogen at different pressures, and have examined their spectra both by eye observations and by photography. The sharp line spectrum of nitrogen is not nearly so striking in brilliancy, number, or sharpness of lines as are those of argon, and careful scrutiny fails to show more than one or two apparent coincidences between lines in the two spectra. Between the spectra of argon and the band spectrum of nitrogen there are two or three close approximations of lines, but a projection on the screen of a magnified image of the two spectra partly superposed will show that two at least of these are not real coincidences.

I have looked for indications of lines in the argon spectra corresponding to the corona line at wave-length 531·7, the aurora line at 557·1, and the helium line at 587·5, but have failed to detect any line of argon sufficiently near these positions to fall within the limits of experimental error.

I have found no other spectrum-giving gas or vapour yield spectra at all like those of argon, and the apparent coincidences in some of the lines, which, on one or two occasions are noticed, have been very few, and would probably disappear on using a higher dispersion. As far, therefore, as spectrum work can decide, the verdict must be that Lord Rayleigh and Professor Ramsay have added one, if not two, members to the family of elementary bodies.

"*The Liquefaction and Solidification of Argon.*" By Dr. K. Olszewski, Professor of Chemistry in the University of Cracow.

Having been furnished, by Professor Ramsay's kindness, with a sample of the new gas, argon, I have carried out experiments on its behaviour at a low temperature and at high pressures, in order to contribute, at least in part, to the knowledge of the properties of this interesting body.

The argon sent by Professor Ramsay amounted to 300 c.c. It was contained in a hermetically sealed glass bulb, so constructed that it could easily be transferred, with no appreciable loss, into the carefully dried and vacuous apparatus in which the proposed experiments were to be performed. The argon with which I was supplied had, according to Professor Ramsay's statement, been dried with phosphoric anhydride; its density was 19·9 ($H=1$); and he thought that at the outside it might contain 1 to 2 per cent of nitrogen, although it showed no nitrogen spectrum when examined in a Plücker's tube.

Four series of experiments in all were carried out, two with the object of determining the critical temperature and pressure of argon, as well as measuring its vapour pressure at several other low temperatures, while two other series served to determine its boiling- and freezing-points under atmospheric pressure, as well as its density at its boiling-point.

A detailed description of these experiments will be given in another place; I shall here give only a short description of the manner in which they were made.

For the first two experiments I made use of a Cailletet's apparatus. Its metallic manometer had been previously compared with the readings of a mercury manometer. As cooling agent I used liquid ethylene, boiling under diminished pressure. The glass tube of Cailletet's apparatus was so arranged that the portion immersed in the liquid ethylene had comparatively thin walls (not exceeding 1 m.m.), so as to equalise the external and internal temperature as quickly as possible.

In both the other experiments the argon was contained in a burette, closed at both ends with glass stop-cocks. By connecting the lower end of the burette with a mercury reservoir, the argon was transferred into a narrow glass tube fused at its lower end to the upper end of the burette, and in which the argon was liquefied, and its volume in the liquid state measured. In these two series of experiments liquid oxygen, boiling under atmospheric or under diminished pressure, was employed as a cooling agent. I made use of a hydrogen thermometer in all these experiments to measure low temperatures.

Determination of the Critical Constants of Argon.

As soon as the temperature of liquid ethylene had been lowered to −128·6°, the argon easily condensed to a colourless liquid under a pressure of 38 atmospheres. On slowly raising the temperature of the ethylene, the meniscus of the liquid argon became less and less distinct, and finally vanished at the following temperatures and corresponding pressures:—

Expt.	Temperature.	Pressure.
1.	−121·2°	50·6 atmos.
2.	−121·6	50·6 ,,
3.	−120·5	50·6 ,,
4.	−121·3	50·6 ,,
5.	−121·4	50·6 ,,
6.	−119·8	50·6 ,,
7.	−121·3	50·6 ,,

In all seven determinations the critical pressure was found to be 50·6 atmospheres; but determinations of the critical temperature show slight differences. In experiments Nos. 3 and 6 less liquid argon was present in the tube than in the other five; in these the volume of liquid exceeded the volume of gas.

In determining the vapour pressures of argon, a tabular record of which is given below, I noticed slight differences of pressure according as I produced more or less of the liquid at the same temperature. This proved that the sample of argon contained an inconsiderable admixture of another gas, more difficult to liquefy; it is doubtless the trace of nitrogen previously referred to. The mean of the seven estimations of the critical temperature is −121°, and this may be taken as the critical temperature of argon.

At lower temperatures the following vapour pressures were recorded:—

Expt.	Temperature.	Pressure.
8.	−128·6°	38·0 atmos.
9.	−129·6	35·8 ,,
10.	−129·4	35·8 ,,
11.	−129·3	35·8 ,,
12.	−129·6	35·8 ,,
13.	−134·4	29·8 ,,
14.	−135·1	29·0 ,,
15.	−136·2	27·3 ,,
16.	−138·3	25·3 ,,
17.	−139·1	23·7 ,,

In Experiments Nos. 9, 10, and 17, the quantity of liquefied argon was very small, for it filled the tube only to a height of 3 to 5 m.m., and in the other experiments the column of liquid argon was 20 m.m. high or more.

Determination of the Boiling and Freezing Points.

Two hundred c.c. of liquid oxygen, prepared in my large apparatus,* was poured into a glass vessel with quadruple walls, so as to isolate the liquid from external heat. After the liquid oxygen had been thus poured under atmospheric pressure, a great part of it evaporated, but there still remained about 70 c.c., boiling under atmospheric pressure. A calibrated tube, intended to receive the argon to be liquefied, and the hydrogen thermometer were immersed in the boiling oxygen. At this temperature (−182·7°*) on admitting argon, no appearance of liquefaction could be noticed, even when compressed by adding a quarter of an atmosphere pressure to that of the atmosphere. This shows that its boiling-point lies below that of oxygen. But on diminishing the temperature of the liquid oxygen below −187° the liquefaction of argon became manifest. When liquefaction had taken place I carefully equalised the pressure of the argon with that of the atmosphere, and regulated the temperature, so that the state of balance was maintained for a long time. This process gives the boiling-point of argon under atmospheric pressure. Four experiments gave the numbers −186·7°, −186·8°, −187·0°, and −187·3°. The mean is −186·9°. which I consider to be the boiling-point under atmospheric pressure (740·5 m.m.).

The quantity of argon used for these experiments, reduced to normal temperature and pressure, was 95·5 c.c.; the quantity of liquid corresponding to that volume of gas was approximately 0·114 c.c. Hence the density of argon at its boiling point may be taken as approximately 1·5. Two other determinations of the density of liquid argon, for which I employed still smaller quantities of the gas, yielded rather smaller numbers. Owing to the small amount of argon used for these experiments, the numbers given cannot lay claim to great exactness; yet they prove that the density of liquid argon at its boiling point (−187°) is much higher than that of oxygen, which I have found, under similar conditions, to be 1·124.

By lowering the temperature of the oxygen to −191° by slow exhaustion, the argon froze to a crystalline mass, resembling ice; on further lowering temperature it became white and opaque. When the temperature was raised it melted; four observations which I made to determine its melting point gave the numbers: −189·0°, −190·6°, −189·6, and −189·4°. The mean of these numbers is −189·6°; and this may be accepted as the melting point of argon.

In the table below I have given a comparison of physical constants, in which those of argon are compared with those of other so-called permanent gases. The data are from my previous work on the subject.

As can be seen from the appended table, argon belongs to the so-called "permanent" gases, and, as regards difficulty in liquefying it, it occupies the fourth place, viz., between carbon monoxide and oxygen. Its behaviour on liquefaction places it nearest to oxygen, but it differs entirely from oxygen in being solidifiable; as is well known, oxygen has not yet been made to assume a solid state.

The high density of argon rendered it probable that its liquefaction would take place at a higher temperature than that at which oxygen liquefies. Its unexpectedly low critical temperature and boiling point seem to have some relation to its unexpectedly simple molecular constitution.

Name.	Critical temperature.	Critical pressure.	Boiling point.	Freezing point.	Freezing pressure.	Density of gas.	Density of liquid at boiling point.	Colour of liquid.
	Below	Atmos.			M.m.			
Hydrogen (H_2)	−220·0°	20·0	?	?	?	1·0	?	Colourless.
Nitrogen (N_2)	−146·0	35·0	−194·4°	−214·0°	60	14·0	0·885	,,
Carbonic oxide (CO) ..	−139·5	35·5	−190·0	−207·0	100	14·0	?	,,
Argon (A_1)	−121·0	50·6	−187·0	−189·6	?	19·9	Abt. 1·5	,,
Oxygen (O_2)..	−118·8	50·8	−182·7	?	?	16·0	1·124	Bluish.
Nitric oxide (NO) ..	− 93·5	71·2	−153·6	−167·0	138	15·0	?	Colourless.
Methane (CH_4)	− 81·8	54·9	−164·0	−185·8	80	8·0	0·415	,,

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* *Bulletin International de l'Academie de Cracovie*, June, 1890; also Wiedemann's *Beiblätter*, xv., p. 29.

* I have re-determined the boiling-point of oxygen, using large quantities of oxygen, and a hydrogen thermometer of much larger dimensions than previously. The registered temperature is 1·3° lower than that which I previously recorded.

Professor RAMSAY exhibited two sealed glass tubes which, he said, contained argon, and handed them round. He said that he had been asked by some of his friends to show them the gas. It was, however, quite invisible.

The PRESIDENT—It will be a satisfaction, I am sure, to anyone present to have one of these tubes in his hand, and to have really handled a glass vessel containing argon.

Dr. ARMSTRONG (President of the Chemical Society)—I am sure, sir, I can say at once that all present to-day who are able to judge of a communication of this kind, and all others outside, will gladly join in the chorus which Mr. Crookes has proposed should be sung. But I should like, speaking more on behalf of the chemists—and I am sure that Professor Ramsay will come over to me for the time and dissociate himself from his colleague—to say that we feel especially indebted on this occasion to Lord Rayleigh, not only on account of the extraordinarily important information which he has placed at our disposal, but more particularly on account of the example which he has set us. You, sir, very fully alluded in your address this year to the patient manner in which Lord Rayleigh had tracked this new element to its home. I feel sure that the words which fell from you will meet with the warmest approbation everywhere where such work can be understood. (Applause). The case contained in the paper is undoubtedly a very strong one. Of course, in the hurry of a meeting like this, it has not been so logically brought forward by the reader of the abstract as it might have been, in order to do it full justice; but yet I think it will be quite clear to all who have listened to him that there is a very strong body of evidence which makes it certain that there is in the atmosphere a constituent which has long been overlooked, and a constituent having most extraordinary properties. The paper is not one which, so far as the experimental facts are concerned, can be criticised here. No doubt it will meet with very considerable criticism throughout the world. People will not be satisfied to take all these statements for granted without checking them, and I have not the least doubt that very soon we shall have abundant confirmations of the correctness of the discovery. But, apart from the facts which are brought forward in this paper, there is a portion which is purely—one almost might say, if I may be allowed the expression on such an occasion—of a wildly speculative character; that is the portion dealing with the probable nature of this new element. Professor Ramsay, in his remarks, in a measure let the cat out of the bag in a way which is not apparent when you read the paper, because it is quite clear that, after all, the authors of this communication are not so entirely satisfied with the evidence to be adduced from the application of the Clausius method for the determination of the atomicity of the gas. I think that they have not sufficiently taken into account, in dealing with this evidence, the extraordinary property that this gas possesses. Nitrogen we know is a very inert form of matter, but we know that the character of nitrogen derived from its study in the atmosphere is of an altogether wrong character. We know perfectly well that, taken as an element and treated as an atom, nitrogen is probably one of the most active forms of matter known to us, and that the great difficulty we have in bringing about its association with fresh elements, when we deal with that gas, arises from its extreme activity — its extreme fondness for its own self. Now, if we can judge anything at all from the properties which we know belong to this new element, it is, I imagine, that it is like nitrogen, but "much more so." It is quite conceivable that the condition which Professor Ramsay pointed out as being the only alternative to the one which is apparently accepted by the authors of the communication is a conceivable condition. It is quite likely that the two atoms exist so firmly locked in each other's embrace that there is no possibility for them to take notice of anything outside, and that they are perfectly content to roll on together without taking up any of the energy that is put into the molecule. There is a great deal to justify a view of this kind. Of course it cannot be discussed independently of what has been said with regard to the new gas being a mixture; but it is quite clear that, as the discussion has gone on, the statements made in the paper are not so thoroughly accepted as one would think that they were. Mr. Crookes evidently wavers very much on this point with regard to there being two elements present, and I gather as much from Professor Ramsay's account. If we think that we are dealing with two gases here on the evidence of the spectroscope, there is no reason why we should not come to the same conclusion with regard to nitrogen and hydrogen. Oxygen, I believe, has three or four spectra, so that the spectroscopic evidence, after all, although it may be in a measure remarkable, does not appear to justify such a conclusion. The great difficulty that we have, I take it, in accepting the conclusion that we are dealing with an element having a molecular weight of 40 and an atomic weight of 40 arises from the difficulty of placing an element of that kind, which practically seems to me to have driven the authors to the conclusion that, possibly, they are dealing with a mixture. The difficulty would be got over, of course, if we were dealing with a complex body, and I think that was rather hinted at by Professor Ramsay when he referred to one of Olszewski's numbers. This low value, high as it is in comparison with that of nitrogen obtained from the density of the liquid, is a reason which would induce us to place it higher up in the scale of elements, and give it a lower weight. Of course these are all matters which must be discussed later on more fully: they are matters which can only be discussed very gradually, as we learn more about this substance. As regards its inactivity, very possibly that may be exaggerated. It is very difficult in a case like this to find out what are the best conditions to make use of. We know perfectly well that, if we were not in possession of the electric spark, we could scarcely have discovered that nitrogen might be combined with hydrogen to form ammonia direct. We know that we can only bring about the combination of the two if we are in a position at once to remove the product; and that sort of thing may well obtain in a case like this. We know very well that there are comparatively few substances which can be directly associated with nitrogen. It is quite likely that here we are dealing with an element which has still fewer affinities, but it does not follow by any means yet—nor do the authors assert such to be the case—that we are dealing with an element which is entirely inactive even in the form in which it is presented to us. This is not the occasion to discuss the matter fully, but these are points which certainly deserve consideration, and they are some of the first points which make this element of such importance and interest to us as chemists. In conclusion, I can only heartily congratulate the authors on having given us this communication.

Prof. RÜCKER (President of the Physical Society)—I think it is very important on this occasion that we should remember that this is a discussion meeting of the Royal Society, a meeting held in this way for the first time, and a meeting at which reporters are present in order that the net result of the discussion shall go out at once to the world. It is therefore, I think, extremely important that we should distinguish as clearly as possible between the various points of doubt which still may remain with regard to the new element which has been described to-day, and the one certain fact which comes out indisputably from the facts which have been laid before us, namely, that in spite of the doubt which may have existed on the matter for the last few weeks or months, we have it now beyond all question—and I quote the words of the President of the Chemical Society in saying so—that it is certain that we have here a new constituent of the atmosphere. What the importance of this is has already been mentioned, and I want once more to emphasize the fact that this central feature stands out quite clear, apart from whether we have one or two, and apart altogether from whether the various physical quantities which have been laid before us to-day have been measured with the accuracy which may be obtained in the future. But there is one particular point to which I should like to refer. It seems to me that one of the most interesting results arrived at from the physical point of view is the fact that the gas is monatomic. Some of us have had the opportunity of seeing the paper before it was read to-day, and we are therefore, perhaps, aware of one or two facts which, I think, were not actually mentioned by Professor Ramsay. One of these facts is that the experiments required to determine the ratio of the two specific heats were made twice over, or many times over, for all I know, but made in two different ways. They were made in a narrow tube, and they were made in a wide tube; and further check experiments were carried on in which other gases were compared with the new element. There can be no possibility of doubt as to a result of this sort when the experiments are carried out by two such men as Lord Rayleigh and Professor Ramsay. The matter is one which admits of no mistake when conducted in this way, and it must be accepted as certain that the element has that particular ratio of specific heats. Well, then the question arises, What follows from this? I think that it has not, perhaps, been quite sufficiently pointed out that, in order that this ratio may be obtained if we are to use the ordinary mechanical theory of gases, it is necessary that the atom with which we are dealing should be regarded as spherical. Of course, I am well aware that our pictures of spherical atoms and the like are, no doubt, only approximations to the truth; but if we are to conceive this atom as consisting of two which are closely united the one with the other, we must nevertheless suppose, from that point of view, that they are so united as to form a sphere. That is only one way of putting it, but, nevertheless, it does create a difficulty which, I think, has not been altogether referred to before. I can only, in conclusion, say that, whatever the effect may be upon the great chemical generalisation of Mendeleeff, that is, after all, an empirical law which is based at present upon no dynamical foundation. If it holds its own in this case, it will, of course, strengthen our belief in it, but, on the other hand, I do not think that it stands on the footing of those great mechanical generalisations which could not be upset without upsetting the whole of our fundamental notions of science.

The President—Among those present I am sure those who understand most of the subject will be anxious to speak. I now ask any person present to make remarks, and especially to ask questions.

Professor Roberts Austen—I should like to say that, when this beautiful discovery was communicated to the British Association, I ventured to point out that it was not too soon to consider its relation to the great metallurgical industries in which air is largely employed. In the Bessemer process alone you take some 10 tons of iron and put it into a vessel called a converter. It is melted, and air is passed through to remove the carbon, silicon, phosphorus, and other impurities. That means that no less than 100,000 cubic feet of air pass through the metal. Therefore 1000 cubic feet of argon have gone somewhere. Now, I have taken Bessemer-blown metal which has been treated with ferro-manganese, and have pumped out forty times its volume of gas, of which one-twentieth was nitrogen. In that nitrogen I have not been able to detect any argon that could not have come from the water which was necessarily used in the manipulation. I have taken a small quantity of air, and abstracted argon from it, and obtained exactly the proportion that the authors say it contains, so I am perfectly certain that the manipulation is correct. But it remains to be seen whether the argon finds its way into the iron, as nitrogen undoubtedly does, and, if it does, whether it stays there, because there are certain peculiarities that make Bessemer metal different from other kinds of steel, and it would be most interesting if we could succeed in tracing it to some of this 1000 cubic feet of argon, which has either passed into the air or into the iron. I should just like to say that I could have wished that the authors of the paper had dialysed the air through india-rubber, and not have merely used clay pipes. As one so long associated with Graham, I can only say how delighted he would have been had he known that his method would have been used by the authors of this paper, one of whom occupies Graham's own chair at University College.

Lord Rayleigh—I have very little to add to the account which my colleague, Professor Ramsay, has given of this research. The research has been, in many respects, a very difficult one. I am not without experience of experimental difficulties, but certainly I have never encountered them in anything like so severe and aggravating a form as in this investigation. Every experiment that one attempts takes about ten days or a fortnight to carry out to any definite conclusion, and the result has been, of necessity, much less progress than we could have hoped for, and many of the questions have been left open which we could have wished to settle. One such question has just been alluded to by Professor Roberts-Austen, namely, the character of the gas transfused through indiarubber. That experiment has been upon our programme, I may almost say from the first, but hitherto time has not been found to carry it out. The difficulties of those parts of the research with which I have been more particularly connected have been very great. The preparation of the gas in sufficient quantity to experiment with at all has been no easy matter, and some of the results, such as those relating to the density of the gas, are consequently not so satisfactory and not so thoroughly elaborated as one could have wished. One point that has been mentioned relates to the argument in favour of the monatomicity of the gas. Of course, what is directly proved by the experiment, if it is good, is that the whole, or nearly the whole, of the energy put into the gas, when it is heated, is devoted to increasing the energy of its translatory motion, and that no margin remains over, as in the case of other gases, to be attributed to intermolecular or interatomic motion. At first sight it seems rather a strange thing that there should be no rotation in the molecules of the gas. How can it be? Can they be without rotation, or can the energy of their rotation be so small as to be negligible in comparison with the energy of the motion as a whole? That is a difficulty which I think has not been thoroughly met hitherto by the cultivators of the dynamical theory of gases; but apparently here we may accept it that no such energy exists, or that no such energy exists in any appreciable degree. Of course that condition is quite well met by the suggestion which has been put forward, and which has also been communicated to us by Professor Fitzgerald, of Dublin, who writes as follows:—

"The reason why the ratio of specific heats of 1·66 is supposed to prove monatomicity in a gas is because in a monatomic gas there are no internal motions of any consequence. Now, if the atoms in a molecule are so bound together that hardly any internal motions exist, it would, so far as specific heat is concerned, behave like a monatomic element. That the atoms in argon may be very closely connected seems likely from its very great chemical inertness. Hence the conclusion from the ratio of its specific heats may be, not that it is monatomic, but that its atoms are so bound together in its molecule that the molecule behaves as a whole as if it was monatomic."

That argument is no doubt perfectly sound, but the difficulty remains how you can imagine two molecules joined together, which one figures roughly in the mind, and I suppose not wholly inaccurately, as somewhat like two spheres put together and touching one another—how it would be possible for such an excentrically-shaped atom as that to move about without acquiring a considerable energy of rotation. That is difficult, and I think the only interpretation is, that the gas is monatomic. No doubt the whole subject is one about which we know exceedingly little, mercury vapour being the only other gas at present which exhibits a similar property. I am not sure that any other point has been raised, but if any questions are asked Prof. Ramsay and myself are quite ready to give further explanations, so far as it is in our power to do so.

The President — I wish to make a remark, not as from the chair, but with reference to the question which is now before us, as to the condition under which the ratio of the specific heats could be exactly $1\frac{2}{3}$rds. I do not admit that a spherical atom could fulfil that condition. A spherical atom would not be absolutely smooth. In other words, it must be a Boscovitch point. Neither can I admit that excessively rigid connection between two atoms could give it the quality of having no capacity whatever for a relative vibratory movement. It would need infinitely stiff connection to give it no capacity for relative vibratory movement; and if it had infinitely stiff relative connection the connection of the two bodies would be indissoluble, and they would remain one. In fact, I think that the only kind of atom that we can conceive as giving, in the dynamical theory of heat, rigorously the ratio of $1\frac{2}{3}$rds for the specific heat is the ideal Boscovitch mathematical point endowed with the property of inertia, and with the other property of acting upon neighbouring points with a force depending upon distance. I have now to ask for any further remarks. I do not wish to closure this most interesting discussion. I hope we shall have further discussion and further questions.

If there are no more remarks and no questions to be put, I desire now, in the name of the Royal Society, to thank the Senate of the University of London for their hospitality on this occasion, a hospitality which I am sure we have all very much enjoyed. I have great pleasure in joining with the President of the Chemical Society and the President of the Physical Society in congratulating Lord Rayleigh and Professor Ramsay on the brilliant success already obtained. (Great cheering.) I join with my brother Presidents in wishing them more and more success in the continuation of their work, and in thanking them heartily in the name of the Royal Society for the communication which they have given us this day. (Cheers).

NOTICES OF BOOKS.

Elementary Practical Chemistry, Inorganic and Organic. By J. T. Hewitt, D.Sc., Ph.D., F.C.S., and F. G. Pope. London: Whittaker and Co.

This pamphlet extends to 42 pp., and is offered at the modest price of ninepence. We fail to find in it any distinctive feature as compared with other elementary treatises of its class. In a table of the solubility of salts we find it stated that lead sulphate is insoluble in water and *acids*. Experiment will convince the student that this is not the case.

The Eighth International Congress of Hygiene and Demography. Resolutions Accepted or Received by the Closing Meeting held September 9, 1894.

This report of the final Proceedings at the International Hygienic Congress is drawn up in a variety of European languages, those of Spain, Portugal, Holland, and Scandinavia being excluded. The English used is of a rather peculiar character, but it may be understood by a comparison with the French and German.

Some of the desiderata laid down concerning the supervision of diphtheria are excellent and deserve to receive legislative sanction at an early date. We fear, however, that they will be energetically opposed where elementary education is conducted on the "payment by results" system (falsely so called). Shall we ever have in every School-board a physician armed with the necessary authority concerning sanitary questions?

Very important was the proposition made by Miss Florence Nightingale on Village Sanitation in India. Many towns and villages there are in a condition which would involve disastrous results even in the cold climate of Britain. In India the co-operation of the natives can scarcely be hoped for as long as superstition leads them to drink the water of holy wells, which are in reality strong sewage, and to use the same waters for cookery and for bathing. In Australia and South Africa the neglect of sanitary precautions is alarming.

In the Sixteenth Section Prof. Than urges that the "composition of bodies should be expressed not as at present in percentages, but according to atomic and molecular quantities as units." The author seems to have overlooked the fact that the substances which have to be analysed for sanitary purposes are, for the most part, not chemical individuals, but mechanical mixtures liable to constant fluctuations.

The questions discussed in the Nineteenth Section, and the views expressed, are too decidedly political to come under our notice.

CORRESPONDENCE.

A REVOLUTION IN VOLTAIC ELECTRICITY.

To the Editor of the Chemical News.

Sir,—Under the above title, in an article in the Chemical News (vol. lxxi., p. 2), Mr. H. N. Warren claims to have discovered a new and remarkable primary battery. It is to be regretted that the discoverer did not give some definite quantitative results obtained from the battery, or else give specific directions for making the battery, so that his results could be verified by others. If, for instance, he had given the capacity in watt-hours per pound of zinc consumed, and the rate of discharge in watts that could be steadily maintained by a battery of specific dimensions or weight, it would have been more interesting to the electrical engineer than the statement that the arc produced between carbon points was "more than the naked eye could bear," or that it heated and melted metals "in quantity."

Such methods of measuring energy are so common with discoverers of batteries destined to "revolutionise voltaic electricity" that the claims are likely to be accepted with some salt.

The claims, both as to cost and electromotive force, taken in connection with his meagre description of the battery, are, to say the least, remarkable. His admission that one of the elements is zinc and the other platinum is significant as to what the economy of the battery can be. And the statement that the "outer cell contains a specially prepared manganic salt" accounts satisfactorily for something over two of his three volts. At the same time it dashes our hopes as to anything new or revolutionary.—I am, &c.,

C. J. Reed.

The Reed Electric Company, 441, Chestnut Street,
Philadelphia, Jan. 16, 1895.

Royal Institution.—On Thursday afternoon, Feb. 14, Mr. L. Fletcher, F.R.S., Keeper of Minerals at the British Museum, will begin a Course of Three Lectures on "Meteorites."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 1, January 7, 1895.

At the opening meeting A. Cornu was elected Vice-President for the year. The inaugural discourse was delivered by the retiring President, Maurice Loewy. The new President is M. Marey.

Preparation of Sprouting Graphites in the Electric Furnace.—Henri Moissan.—The sprouting may be ascribed to an abrupt escape of gas expanded by heat. The author's experiments prove that the sprouting graphites produced in laboratories may be as numerous as those met with in nature. They will also enable us to explain the formation of the natural sprouting graphites, some of which yield, as it is known, ashes most commonly very rich in iron oxide. These graphites seem to have been produced at a high temperature, without great pressure, in the midst of masses of iron which seem to have disappeared from the action of gaseous acids. Graphite resists most chemical agents. At dull redness it is not affected by watery vapour and air. It is thus found separated from its metallic gangue, and has formed masses where it has been disseminated in the rocks. From all these experiments we may conclude that a sufficient rise of temperature converts any variety of carbon into graphite, whether sprouting or not sprouting. Certain compounds, in particular iodised substances, may determine this transformation at a lower temperature, as it has been shown by Berthelot. These are reactions comparable to those of iodine upon ordinary phosphorus, which admit of polymerisation being produced earlier without modifying the general direction of the phenomenon.

Nomination of a Correspondent for the Section of Mineralogy.—M. Matheron was elected by a large majority, *vice* Scacchi, deceased.

A Special Committee has been nominated to consider a memoir by J. H. West, on the question "Why do cats always fall on their feet?"

Utilisation of the Temperature of the Critical Point of Liquids for the Recognition of their Purity.—Raoul Pictet.—We find, from the instances given, that the critical point is much more sensitive than the boiling-point. The displacement is always in the same direction for the temperature of the critical point and the point of ebullition. The addition of liquids which are more volatile and dissolve readily lowers the temperature, as in the case of aldehyd added to pental. On the contrary, the admixture of pure chloroform, boiling at 61° with alcohol, which is less volatile, lowers the temperature of the critical point. Chlorethyl boiling at +11° has its critical point raised by the addition of a few drops of alcohol which boils at 78·8°. These experiments have been continued on ether, alcohol, and mixtures of solids in solution.

Qualitative Separation of Nickel and Cobalt.—A. Villiers.—Already inserted.

Revue Universelle des Mines et de la Metallurgie.
Vol. xxviii., No. 2.

Composition of Atmospheres which Extinguish Flame. — Prof. Frank Clowes, D.Sc. — A paper read before the Royal Society.

Electricity in Chemical Industries. — Electricity is more and more employed in chemical industry in the moist way, for the production of potassa, soda, chloride of lime, potassium chlorate, ozone, the chromates and permanganates, white lead, hydrogen and oxygen, &c. The establishment at Griesheim, near Frankfort, treats KCl in order to produce potassa and calcium chloride. The secret lies in the nature of the diaphragms which separate the kathodes from the anodes, and which allow the electrolysis to be effected without increasing the resistance, and consequently the tension. The electrodes are in general of platinum, retort-coke, lead peroxide, iron sulphide, phosphides or silicides, and polarisation is combatted by chemical and mechanical means. Kathodes of mercury allow of the electrolysis of solutions of KCl even without diaphragms. On treatment with hot water the amalgam yields caustic potash and mercury. The Associated Works at Leopold's Hall use parchment-paper as a diaphragm. To the liquid at the anodes they add 2 per cent of calcium or magnesium chloride, which, on contact with the alkaline liquid of the kathodes, forms a preservative deposit of basic chlorides upon the parchment-paper.—*Berg und Hutten Zeitung* (No. 48, 1894).

MISCELLANEOUS.

City and Guilds of London Institute.—The Executive Committee of the City and Guilds of London Institute have awarded the first Salters' Company's Research Fellowship for the encouragement of Higher Research in Chemistry in its relation to Manufactures to Martin O. Foster, Ph.D., F.C.S. Dr. M. O. Foster was a student at the City and Guilds Technical College, Finsbury, during three sessions (1888—1891), and subsequently graduated Doctor of Philosophy (*magna cum laude*) at the University of Würzburg. For several months he has been engaged in investigating some new derivatives of camphor in the Research Laboratory of the City and Guilds Central Technical College, and by the aid of the Salters' Company's Research Fellowship he proposes to pursue this line of work.

Institute of Chemistry of Great Britain and Ireland.—Names of the candidates who passed the examination held in January, 1895:—A. E. Bell, Owens College, Manchester, and Royal College of Science, South Kensington; C. S. Ellis, Owens College, Manchester, and University College, Aberystwith; M. O. Forster (Ph.D., Leipzig), Finsbury Technical College; J. Lones, Mason College, Birmingham, and Registered Student under A. E. Tucker, F.I.C.; G. H. Russell, Yorkshire College, Leeds; W. H. Sodeau, King's College, London; W. L. Sutton, University College, London; W. G. Young, University College, London, and Registered Student under W. C. Young, F.I.C. Examiners:—Professor Wyndham R. Dunstan, M.A., F.R.S., F.I.C., and Thomas Fairley, F.I.C.

Study on Oil of Cananga.—A. Reychler.—The density of this essential oil at 21° is 0·9058, and the index of refraction $n = 1{\cdot}49655$. Its levo-rotation $[\alpha]_D = -28{\cdot}5°$. Its compostition is C, 85·68; H, 11·81; O, 2·51. Oil of cananga has a great resemblance to ylang-ylang, but it is clearly distinguished from the latter by containing a much larger proportion of sesqui-terpene. [It is to be regretted that French scientific journals often insert a memoir without indicating clearly at the beginning or the end that it has already appeared in some other journal or has been read before some learned society].—*Bull. Soc. Chimique.*

Novelist's Chemistry.—We have occasionally had occasion to twit contemporary novelists with striking and sometimes amusing ignorance of anatomy and physiology. Their chemistry is not always above suspicion; witness the late Mr. Florence, who makes prussic acid play a lethal *rôle* in one of his stories, the acid in question having been stolen from one of the "carboys standing at the door of the drug store." In one of the Christmas stories the detection of the murderer was contributed to by a witness having accidentally "caught a whiff of the strychnine" on applying his nose to the bottle. Sharp nose that!—*Medical Press.*

The Solubility of Phenyhydrazin in Watery Solutions of the Alkaline Salts of the Sulphinic, Sulphonic, Fatty, and Biliary Acids.—Robert Otto.—The author finds on examining the phenylhydrazin salt of β-naphthylsulphinic acid, prepared from its constituents in a solution of methyl-alcohol, that the product is soluble in potassa lye without separation of phenylhydrazin. It appeared that the phenylhydrazin salt is not capable of decomposition by aqueous potassa lye, is not decomposed with precipitation of phenylhydrazin, because the base, soluble in water only in a slight degree, and almost insoluble in concentrated potassa lye, is readily soluble in an aqueous solution of alkaline naphthylsulphinate. If phenylhydrazin is added to such a solution it dissolves completely on shaking, forming a liquid which is miscible with phenylhydrazin in any proportion. Phenylhydrazin is insoluble in a solution of sodium ethylsulphinate. The same behaviour was observed with phenylhydrazin in contact with aqueous solutions of the alkaline salts of the aromatic sulphonic acids, the higher fatty acids (soaps), and the biliary acids. The author mentions an analogy between phenylhydrazin and the phenols. Like the former base these compounds become soluble in water by the mediation of soap, sodium salicylate and kresotinate, sodium kresol, &c. The disinfectants sold under the names sapocarbol, lysol, salveol, &c., belong to this class.—*Berichte*, xxvii., p. 2131.

The Oyster Panic.—According to *Science* the origin of the present panic is as follows:—Professor H. W. Coun described in the *Medical Record* of December 15th last twenty-six cases of typhoid which had occurred in October and November at the Wesleyan University. The first cases among the students appeared on October 20th, and seemed to be connected with the fraternity suppers held on October 12th. The water supply was tested, and the plumbing was examined with negative results. Nothing suspicious was traced in the food, save in case of raw oysters, obtained, as we learn by all the three fraternities, from one and the same dealer. These oysters had all been obtained from the deep water of Long Island Sound, and had been laid in the mouth of a fresh water creek to fatten. This fattening is a process of questionable honesty, since it consists merely in causing the mollusk to absorb fresh water by osmosis, thus increasing its bulk without adding to its proportion of nutritive matter. It was found that within 300 feet of the place where the oysters had been laid to fatten was the outfall of a private sewer, leading from a house where there were at the time two cases of typhoid fever. It is possible that other similar cases may have arisen elsewhere, but there is no evidence that oysters from clean water can contain the bacilli of typhoid. One inference may be drawn with certainty, that is that fishes, mollusks, and crustaceans may be highly dangerous if obtained at or near the outfall of polluted rivers, of sewers, or in places where sewage sludge is thrown into the sea. In other words, we see the impolicy of all schemes for the treatment of sewage which turn on its discharge, or the discharge of its deposits, into the sea.

MEETINGS FOR THE WEEK.

Monday, 4th.—Society of Chemical Industry, 8. "Some Matters of Interest in the Manufacture of Coal-gas," by Lewis T. Wright, C.E, F.C.S.
—— Medical, 8.30.
Tuesday, 5th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
—— Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Society of Arts, 8. "Drawing for Process Reproduction," by Gleeson White.
Wednesday, 6th.—Society of Arts, 8. "The Labour Question in the Colonies and Foreign Countries," by Geoffrey Drage.
—— Geological, 8.
Thursday, 7th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "George Eliot, the Humourist as Poet," by W. S. Lilly, M.A.
—— Chemical, 8. "The Electromotive Force of an Iodine Cell," by A. P. Laurie, M.A. "The Action of Heat on Ethylic β-Amidocrotonate," by Dr. Collie. "The Acidimetry of Hydrofluoric Acid," by Prof. Haga.
Friday, 8th.—Royal Institution, 9. "The Anti-toxin Serum Treatment of Diphtheria," by G. Sims Woodhead, M.D.
—— Astronomical, 3. (Anniversary).
—— Physical, 5. (Annual General Meeting). "An Exhibition of Simple Apparatus," by W. B. Croft, M.A. "On the Tin Chromic Chloride Cell," by S. Skinner.
Saturday, 9th.—Royal Institution, 3. "Hansel und Gretel" (with musical illustrations) an opera by E. Humperdinck, by Sir Alexander Campbell Mackenzie, Mus. Doc.

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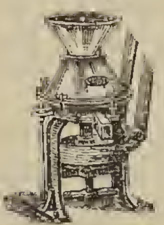

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THE CHEMICAL NEWS.
Vol. LXXI., No. 1837.

ARGON—A SUGGESTION.

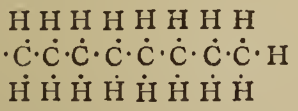
By G. JOHNSTONE STONEY, M.A., D.Sc., F.R.S.

In the examination of argon we are still at the stage of being engaged in the search for what it really is; so that it is not useless at this stage to set down all the *possible* alternatives.

And first, with respect to the ratio of the specific heats and what it implies, viz., that the energy of the "internal" motions—of motions within the individual molecules—is small. There is, as regards this, another alternative besides those presented at the meeting of the Royal Society, which is that the mass of the molecule may consist of a large mass comparatively quiescent and a small mass in active motion. In this case, as well as in those stated at the meeting, the energy involved would be small; and we should, moreover, have a state of things very much more consonant with the fact that argon emits two complex and bright spectra.

Such "internal" activity involving little energy is not unknown. It is, in fact, what occurs in the familiar phenomenon of phosphorescence, where a body has had such motions set up in some part of each molecule as are capable of emitting light for a long time, but which are so isolated from the rest of the molecule that they do not share their energy with it so as to raise the general temperature.

It may be objected that if the molecule consist of one predominant mass associated with one or more small masses, the predominant mass will absorb energy by rotating; but this is based on the supposition that it is a rigid body. Now we must remember that, though this conception of rigid bodies is so much the most convenient to the mathematician that it is universally adopted in the dynamical investigation, nevertheless such bodies are *impossible* from the physicists' standpoint, and do not exist in nature. Who that considers the connections can doubt that a molecule of the normal paraffin C_8H_{18}, which may be represented by—



$$\begin{array}{cccccccccc} & H & H & H & H & H & H & H & H & \\ H\cdot & C\cdot & C\cdot & C\cdot & C\cdot & C\cdot & C\cdot & C\cdot & C\cdot & H \\ & H & H & H & H & H & H & H & H & \end{array}$$

is more like a long flexible thread than a rigid sphere? Now, it is easy to conceive that at the close of an involved struggle between two such molecules protracted over a time which is long when compared with other molecular activities, the conditions may be such when they part that they will sail off from one another without much rotation having been set up. Where we are misled is by the false analogy of rigid bodies, and especially by thinking of the prolonged encounter that takes place in nature with all its complex incidents, as a mere collision!

To return to our illustration. It is quite conceivable that during the journeys of such a molecule as that of the vapour of the above paraffin between its encounters, the two end atoms, or the parts of them which carry their electrons,* may be swinging about violently, while the rest of the system travels along without much internal agitation.

This particular illustration has been selected because it seems *possible* that by the discovery of argon we have been brought within grasping-distance of a much greater discovery; in fact, that it may in reality prove to be a compound of one of the six missing elements which lie between hydrogen and lithium—perhaps a compound somewhat like the above paraffin.

Assuming George Darwin's account of the origin of the moon, we must presume that as the moon and earth cooled down they evolved similar atmospheres, but that the potential of gravitation on the moon is too small to have enabled it to prevent the occasional escape of molecules of water, nitrogen, oxygen, and carbon dioxide; so that it has now been left without its atmosphere. In a discourse delivered before the Royal Dublin Society on December 19, 1870, the present writer called attention to this explanation of the non-existence of atmosphere on the moon, and pointed out the fact that these gases having been able to escape from the moon, involves as a necessary consequence that a body with the earth's potential of gravitation and velocity of rotation must be unable to prevent the escape of free hydrogen from its atmosphere. Hence we should have now no hydrogen on the earth were it not for the circumstance that hydrogen entered extensively into combination with other elements, and thus forms part of molecules too massive to be able to escape from the earth. The earth, in fact, is only able to hold its large stock of hydrogen as constituents of such compounds as water, ammonia, hydrochloric acid, of organic substances generally, and of some minerals. But except in a state of combination, the earth is not competent to retain hydrogen.* The six other elements between hydrogen and lithium seem not to have been able to enter into, or to remain in, combination under the conditions that prevailed at some stage of the earth's past history, and so then escaped—unless, possibly, a compound of some of them may yet be found.

Let us, for convenience, name them as in the accompanying Mendeleeff table.

Argon, then, may turn out to be a compound of one of these; and of them the most probable is perhaps infra-carbon. Silicon shows a slight aptitude for combining with hydrogen, and the hydride of silicon is a very active body. Carbon forms with avidity compounds with hydrogen that are so inert that one great series of them has been called "paraffins," from *parum affinis*. If this property is as much more intense in infra-carbon than in carbon, as it is more intense in carbon than in silicon, it may well result in producing a compound as impassive as argon.

Assuming that the atomic weight of infra-carbon is about 2½ or 3, then if it forms compounds similar to those of carbon, argon may be analogous to one of the paraffins C_7H_{16}, C_8H_{18}, C_9H_{20}, or to some other hydrocarbon of the fatty series, or to hydrocarbons of the benzene series, or to such compounds as naphthalene, $C_{10}H_8$; diphenyl, $C_{12}H_{10}$; turpentine, $C_{10}H_{16}$. It may even, though with less probability, be analogous to a monatomic alcohol, such as $C_4H_9{\cdot}OH$ or $C_5H_{11}{\cdot}OH$, or to some other compounds, and its inertness may be such that even substitution derivatives may be very difficult to produce.

A mere speculation such as this is only allowable under circumstances like the present—while we are feeling

Hydrogen	Infra-beryllium	Infra-boron	Infra-carbon	Infra-nitrogen	Infra-oxygen	Infra-fluorine	
Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine	
Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Chlorine	
&c.	&c.	&c.	&c.	&c.	&c.	&c.	&c.

---

* Electron, the fixed charge of electricity, the same in all cases, which is associated with each chemical "bond."

* The same method applied to Mars leads to the conclusion that it is improbable that the vapour of water can be retained by that planet, in which case we must look to some substance of greater density, such as carbon dioxide, as the material which produces the snow caps and the long streaky fogs (probably following valleys) which are from time to time seen upon Mars.

about for what argon really is. In one respect argon behaves very differently from the organic compounds of carbon, in that it is not decomposed by heat. This seems a natural consequence of the fact which has been brought to light by the ratio of its specific heats, viz., that but a small part of its heat energy takes the form of events going on within its molecules. Besides, infra-carbon is quite as likely to approximate to silicon in some of its properties as to carbon. But, above all, the hypothesis that argon is a compound has this great recommendation, that it does not involve any interruption of Mendeleeff's law, which, though only empirical, is probably true. The writer therefore hopes that this alternative possibility will be investigated along with the other, and perhaps less probable, ones that were produced at the meeting of the Royal Society.

THE NOMENCLATURE OF THE PENTOSES AND PENTOSANS.

By C. F. CROSS.

Dr. Stone's rejoinder (Chemical News, lxxi., p. 40) to my suggestion of a more neutral designation, for certain purposes, of the furfural-yielding carbohydrates, although based on a more or less obvious misapprehension of the issue which I intended to raise, leaves me no option but to elaborate the point in reply. Since my critic remarks, "it is hardly possible" that I "should be unacquainted with the terms 'pentoses' and 'pentosans' in common use to designate these bodies," there appears to be some residual apprehension of my aiming, in ignorance, a quixotic thrust at the systematic and "official" terminology of the carbohydrates. Such an intent I need not disclaim. The next paragraph of the criticism contains the fundamental mis-statement upon which the whole issue turns, and it is a wider one than appears to have been recognised. "The furfural reaction, as applied to carbohydrates, is given only by the pentatomic sugars or by certain amorphous substances which upon hydrolysis yield one or other of these sugars." On this point the author must be referred to categorical evidence to the contrary contained in recent publications (Cross and Bevan, *Ber. Chem. Gesell.*, xxvi., 2520—2533; xxvii., 1061—1065). There are, in fact, a large number of celluloses of "carbohydrate" formula, or approximately so, which give yields of furfural of from 2 to 15 per cent, which at the same time do not give the characteristic reaction (with phloroglucinol) of the pentoses and pentosans, and are further differentiated from the latter by comparative resistance to hydrolysis.

To take the controverted point for a moment out of a region which appears to involve too much of the personal element, the following parallel case may be given:—The oxidation (HNO_3) of galactose groups to mucic acid was regarded until recently as a positive and exclusive diagnosis of their presence in carbohydrates of unknown composition. It has now been shown that the methyl-hexoses are similarly oxidised to this acid. Supposing the hexoses were always referred to under a systematic terminology, under which the galactoses might be distinguished as γ-hexoses. The application of the logic of Dr. Stone's contention would lead to the extension of this term to the methyl-hexoses. Thus, if furfural-yielding carbohydrates = pentoses; mucic acid yielding carbohydrates = γ-hexoses; then pentoses = C_5-aldoses with certain hexose derivatives, &c., γ-hexoses = galactoses, methyl-hexoses, &c., which propositions are absurd. On the other hand, a neutral term such as mucose or furfurose, instead of conflicting with the systematic description, merely groups together bodies of varying composition under a common characteristic of decomposition, having sufficient significance to make it a subject of continual reference.

Having just completed a monograph on cellulose (Cross and Bevan, "Cellulose," Longmans, 1895), it has been found necessary to make free use of the terms "furfural-yielding carbohydrates," "furfural-yielding complex," &c., in describing constituents of the permanent tissues of plants, having this property in common with the pentosans, but differing in other equally characteristic reactions, and on general physiological grounds with equal probability hexose derivatives.

A year or two ago we (Cross and Bevan) expressly maintained this view of the origin of these furfural-yielding constituents of plants. Stone and de Chalmot, in approaching this subject from the point of view of the pentoses and pentosans, and using these terms as interchangeable with the above phrase description, were undoubtedly misled into the view that the pentoses were direct products of assimilation. De Chalmot has now established as the issue of an important series of investigations, and in opposition to his earlier conclusions, that these furfural-yielding constituents are products of metabolism, and derived through oxidation processes from the hexoses.

Approaching this physiological question from the point of view of systematic chemistry, there appeared, *à priori*, no cogent reason why the plant should not build up C_5 or C_7 aldoses.

Coming to the same subject under consideration of the general prevalence of the hexoses — their liability to graduated oxidation—and such products tending also to the $R.C_4O$ (furfural) condensation, we gave preference to the opposite hypothesis. We also have held the opinion that those specialists who have done such excellent work in the pentose group would not have taken up a position in regard to the assimilation problem from which they have withdrawn, but for the undue influence of terms and the assigning of final significance to a reaction of decomposition.

My suggestion still is that some neutral term should be used to designate "furfural-yielding carbohydrates" (or their immediate derivatives) not yet ascertained to be pentosans, and from their properties generally probably containing furfural-yielding groups other than those of pentose configuration.

ON THE PROTOMORPHIC STATE. ZINC AND MANGANESE SULPHIDES.

By A. VILLIERS.

We have recently pointed out certain reactions of nickel and cobalt sulphides, and have indicated some new properties of these substances which seem to us to show that at the moment of their formation they must exist in a different state from that in which we know them when once formed. This condition we propose to denominate as the *protomorphic state.*

The reactions produced in this state by the nickel and cobalt sulphides are merely an instance of reactions a certain number of which are already known, and which may be produced by bodies before they have acquired their ultimate properties, after having undergone one or more transformations probably corresponding to condensations with liberations of heat often manifested by phenomena of crystallisation.

These transformations are immediate and cannot be demonstrated by calorimetric methods, but only by chemical reactions effected at the moment of their formation. This is the case with nickel sulphide. They are either produced but slowly, say, in a few minutes, and may then be shown by the liberation of heat which goes on after the bodies constituting the original system have been brought in contact, or during several days, several years, occasionally during a time too long for the direct observation of the corresponding liberation of heat. In this latter case, which is that of a great number of precipitated oxides and salts, we may at any moment form an idea of the actual state of the substances, whether by the quantities of heat evolved when they are brought to a final, definite condition, or by the differences observed in their chemical properties.

The *protomorphism* of the metallic sulphides may be manifested by this latter method in a very great number of sulphides other than those of nickel and cobalt, and the precipitated sulphides may produce certain reactions interesting from a twofold point of view, since they indicate the existence of novel compounds, and are sometimes capable of analytical applications.

Zinc Sulphide.—The transformation of zinc sulphide is not immediate in the cold, like those of nickel and cobalt sulphides. It is very rapid in heat, but it goes on at common temperatures for several hours or more. This may be manifested by the action of the alkaline sulphides.

Professor Thomsen (*Berichte*, xi., 2044) has shown that sodium sulphide gives with a solution of zinc sulphate a precipitate of zinc sulphide; but if we substitute for the alkaline sulphide a hydrosulphate of sulphide, the zinc sulphide is still formed if we employ the latter only in equivalent quantity; but if we go on adding twice the quantity of hydrosulphate of sulphide, we obtain no precipitate, but a limpid or opalescent liquid which yields a precipitate of zinc sulphide or hydrosulphate if we add either soda or an acid.

The soluble compound of zinc sulphide and of alkaline hydrosulphate of sulphide, comparable to that of zinc oxide and potassium hydroxide, may be produced still more decidedly as follows:—

If into the alkaline liquid obtained by pouring a solution of zinc sulphate into soda until the former no longer re-dissolves, we pass a stream of hydrogen sulphide, we find that the first bubbles of the gas occasion the precipitation of the zinc as sulphide. If we continue the introduction of the gas this precipitate re-dissolves, and we obtain in a few moments a liquid completely limpid, if the solution is sufficiently dilute, *e.g.*, with a liquid prepared with solutions of soda and zinc sulphate at 10 per cent, and then diluted to one-tenth. The weak acids and alkalis still precipitate zinc sulphide; the same precipitation is produced on boiling. We have, therefore, a combination of zinc sulphide and sodium sulphide hydrosulphate.

It is easy to show, on slightly modifying the conditions of this experiment, that zinc sulphide recently precipitated undergoes a transformation.

If, after having introduced the first portions of sulphuretted hydrogen so as to precipitate zinc sulphide, we do not prolong the action of the gaseous current, and leave the mixture at the ordinary temperature of 15° to 20° after having carefully stoppered the vessel in which the precipitation has taken place, we find that after the lapse of some hours the zinc sulphide is no longer capable of being re dissolved by the action of a further quantity of hydrogen sulphide, however long we continue to pass the gas into the liquid.

This transformation may be immediate or slow according to the conditions which we shall shortly define.

Zinc sulphide precipitated in its soluble modification in sodium sulphide hydrosulphate is always amorphous. In its insoluble modification we have always found it crystalline.

The use of sodium sulphide hydrosulphide enables us to separate the amorphous sulphide from the crystalline sulphide, and to follow the march of the transformation when it takes place in a progressive manner.

We shall make it remarked, from the analytical point of view, that the above facts show how in the separation of metals we should use only alkaline sulphides and not hydrosulphates of sulphides, especially when working in the cold, and that we cannot substitute for the use of the alkaline sulphides that of hydrosulphuric acid by passing the gas into the alkaline liquid.

We see also that there may occur a source of error in the qualitative recognition of zinc, and that the precipitation of zinc sulphide by sulphuretted hydrogen in an alkaline liquid may escape observation. It is therefore well to effect this precipitation in a liquid supersaturated with acetic acid.

Manganese Sulphide.—The protomorphism of manganese sulphide cannot be manifested by the foregoing reaction, at least under the conditions in which we have been able to manifest the protomorphism of zinc sulphide.

We may even separate manganese from zinc by passing a current of hydrogen sulphide for some minutes into a liquid containing ammonia and ammonium chloride, avoiding excess of the two latter. If the dilution is sufficiently great, manganese sulphide will be alone precipitated in the cold, whilst the zinc sulphide may be found in the filtrate, and may be separated by an addition of acetic acid.

We must remember that manganese sulphide may occur in at least two very different aspects, either of a flesh-colour or of a green. The two modifications correspond to different states of hydration. The transformation of the former into the latter was discovered by Berzelius, and has been studied by Muck, and by P. de Clermont and H. Guiot. The former state may be compared to amorphous zinc sulphide, and the latter to crystalline zinc sulphide. The transformation of manganese sulphide seems to ensue in conditions analogous to those of zinc sulphide, but less easily—*e.g.*, at higher temperatures or in more concentrated solutions.

The negative indication here manifested is no proof that ordinary flesh-coloured manganese sulphide does not in turn result from the transformation of a sulphide existing in an earlier protomorphic state.—*Comptes Rendus*, cxx., p. 97.

NOTE ON THE

ESTIMATION OF SOLUBLE PHOSPHATE.

By VINCENT EDWARDS, F.C.S.

As the correct estimation of soluble phosphoric acid in manures is, now more than ever, a matter of importance, I venture to submit the following remarks, which may be of interest to chemists in manure works who desire rapid and accurate results.

It occurred to me that the differences sometimes found in the determination by competent chemists might be due to the length of time which was allowed for the precipitate of ammonio-magnesium phosphate to settle, and I therefore carried out the following experiment to clear up the point:—

I had in hand a sample of high superphosphate, known to contain between 19 and 20 per cent of P_2O_5, soluble in water; and having weighed out two quantities of 1 grm. each, treated them precisely alike, with successive washings of cold, and finally hot water, in the manner generally employed. To the clear filtrate of each 50 c.c. of citro-magnesic solution (Sutton) was added, followed by excess of ammonia, and the contents of each beaker being vigorously stirred, the precipitates were allowed to settle—No. 1 for one hour and a half, No. 2 for forty-eight hours. The precipitates were collected, washed with dilute ammonia, dried, and ignited as usual. The results were found to be — No. 1, 19·20 per cent; No. 2, 19·14 per cent P_2O_5.

From these results it would appear that the length of time in which the precipitate is allowed to settle is not of much importance; but it is interesting to note that the longer period gives slightly the less result.

As I had reason to know that the above figures are accurate, it would seem well to allow about two and a half hours for the precipitate to subside. This would not only permit the whole of the ammonio-magnesian phosphate to form, but give it also full time to settle, and render the subsequent operations more satisfactory. Two hours and a half is not long, and with an early start permits several accurate results to be returned in the evening.

It is well to add that excess of ammonia in the beaker during settling is most essential, the solubility of the precipitate being somewhat marked if this is not attended to. The complete washing of the collected precipitate is to my mind also very important; any neglect of this is a greater cause of error than anything else.

Lawes' Works, Barking, Essex,
January 22, 1895.

DERIVATIVES OF DIAMIDE WITH A CLOSED ATOMIC GROUPING.

By TH. CURTIUS.

(Continued from p. 47).

Treatise II.—*On Pyrazolin and some of its Derivatives.*

By F. Wirzing.

Hydrazin hydrate acts simultaneously in the cold upon akrolein, forming pyrazolin. The akrolein hydrazin first formed is at once transposed into pyrazolin. Akrolazin is not formed.

Pyrazolin is a volatile liquid of a decidedly basic character. It combines with the mineral acids to form salts permanent in the air. It has also the nature of a feeble acid, and it forms double compounds with the metallic salts. Pyrazolin shows its nature as an atomic chain combined in a ring by its ready transition into pyrazol in presence of bromine and by its great stability with concentrated mineral acids.

In its decomposition by acids there is a formation of hydrazin and β-lactic aldehyd. Its boils without decomposition at the ordinary pressure of the atmosphere. Pyrazolin is energetically attacked by oxidising agents with development of gases. Permanganate reacts at once in the cold. Gold chloride, ferric chloride in a neutral solution in the cold, and platinum chloride in heat, attack pyrazolin energetically with liberation of gases. It does not reduce Fehling's solution even on ebullition. Ammoniacal solution of silver in heat is gradually reduced by the free base to metal, but solution of gold chloride at once.

Pyrazolin does not display the so called pyrazolin reaction of Kron's (1)-phenylic pyrazolin derivatives. (Colouration in very dilute solutions by oxidising agents). Its salts gives in aqueous solutions a very characteristic reaction, by means of which they can be readily distinguished from those of pyrazol. In the most dilute solutions they colour lignin (woody fibre) a most intense dark yellow.

Pyrazolin takes a dark yellow colour with nitrous acid, but no nitroso-compound has as yet been isolated. It readily combines with benzaldehyd with the elimination of water. With diabenzene salts it combines to form pyrazolinazobenzene substances of a splendid red colour. Neither of these reactions is obtained with pyrazol, but with pyrazolon.

The author adds a comparative table of the characteristic reactions of pyrazol, pyrazolin, and pyrazolon.

(3)-methyl-(5)-dimethylpyrazolin is readily obtained by the action of hydrazin hydrate upon mesityl oxide in the cold. The same substance is formed, according to Curtius and Foersterling, by the transposition of bis dimethylazimethylen by means of maleic acid. It is a colourless oil of a powerful odour, and a decided basic character. It combines with acids, bases, and salts. The heated vapour of the free base explodes on access of air with a display of fire. Its form no azo-dye with azobenzene salts,—in contrast to pyrazolin. It gives precipitates with the solutions of various heavy metals.

During the action of phenylhydrazin upon akrolein there is formed, in addition to (1)-phenylpyrazolin, a second substance of the empirical formula $C_{24}H_{34}N_6O_{12}$.

Benzaldehyd and (1)-phenylpyrazolin combine only in equimolecular proportions. The product benzalphenylpyrazolin seems to exist in two modifications.

Nitrous acid acts upon (1)-phenylpyrazolin with formation of a brick-red isonitroso-compound,—

$$C_6H_5.C_3H_3N_2 : NOH.$$

Diazobenzene salts form with phenylpyrazolin a purple-red basic colouring matter, $(C_6H_5.N_2C_3H_4).N_2C_6H_5$, which yields a dark steel-blue hydrochlorate. The acetic solution of the pigment is reduced by zinc-powder.

The behaviour of phenylpyrazolin with hydrochloric acid is very peculiar. There is formed a compound of 2 mols. phenylpyrazolin with 1 mol. hydrochloric acid, from which the original base cannot be again separated. This product has totally modified properties, and it may be regarded as a bis-phenylpyrazolin. The constitution of the base is not yet known with certainty.

Bis-phenylpyrazolin gives red precipitates with diabenzene salts, with nitrous acid or bromine.

Allyliodide and hydrazin hydrate were caused to react upon each other in the expectation of thus arriving at pyrazolidin. The research had not the desired result.

Besides diammonium iodide as the main product, there was obtained a substance, $C_9H_{17}N_2.I$, which may be regarded as diallylpyrazolidin iodide, or as a triallylhydrazin iodide.

Pyrazolin is a colourless liquid of a characteristic faintly aminous odour which reminds us of cacao. It forms a mist with vapours of hydrochloric acid. At 144°, and at a pressure of 760 m.m., it boils without decomposition. It is volatilised along with the vapours of water and of ether. It mixes with water and alcohol in all proportions. Its composition is $C_3N_2H_6$.

The author next describes the compounds of pyrazolin with hydrochloric acid, $C_3H_6N_2.HCl$, with sulphuric acid, its chloroplatinate, $(C_3H_6N_2.HCl)_2.PtCl_4$, and its picrate.

The behaviour of pyrazolin with acids proves that it cannot be an akroleinhydrazin.

On treating pyrazolin in a reflux refrigerator with concentrated alkaline lyes, about 10 per cent of the nitrogen present is split off.

Pyrazolin is very sensitive to oxidising agents, as it has been mentioned above. The behaviour of bromine with pyrazolin or pyrazolin hydrochlorate is distinct, as they are totally converted into pyrazol.

The demonstration that the base formed from akrolein and hydrazin hydrate is a pyrazol hydride is given by the conversion of the base itself, or of its hydrochlorate into pyrazol by means of bromine in a solution into chloroform, as well as by the production of brompyrazol from pyrazolin hydrochlorate (in presence of Br ?) in an aqueous solution.

(To be continued).

Production of the Kathode Rays.—Jos. de Kowalski.—A full abstract of this memoir would require the three accompanying figures. The conclusions reached by the authors are, that the production of these rays is not connected with the discharge from the metallic electrodes through rarefied gases. They are produced whenever the so-called primary luminosity attains a considerable intensity, or, in other words, whenever the density of the lines of the current is sufficiently considerable. The direction of their propagation is that of the lines of the current in the portion where the rays are produced in the direction from the negative pole to the positive pole.—*Comptes Rendus*, cxx., No. 2.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 17th, 1895.

Dr. ARMSTRONG, President, in the Chair.

MESSRS. Cecil Cooke Duncan and Robert W. Buttermer were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Thomas Bennett Case, B.A., 82, James Street, Dublin; Henry Fairrie, 63, Parkfield Road, Liverpool; Herbert Edward Gardner, Lyonsdown Vicarage, New Barnet; Henry Tresawna Gerrans, M.A., 20, St. John Street, Oxford; George Goldfinch, Hendon, N.W.; Edgar Joseph, 42, Brondesbury Road, Kilburn, N.W.; Henry R. Le Sueur, B.Sc. (Lond.), Chemical Laboratory, St. Thomas's Hospital, S.E.; Robert Meldrum, 27, Lansdowne Road, S.W.; Henry Edward Niblett, B.A., Eldon Lodge, Hewlett Road, Cheltenham; Harry James Powell, 530, Lordship Lane, S.E.; Herbert Lewin Robinson, 9, Lloyd Street, W.C.; Harry Wilson, 146, High Street, Southampton.

The certificate of the following candidate, proposed by the Council under By-law 1 (3), was also read:—

Edward Herbert Hill, Colonial Bank of New Zealand, Dunedin.

The following is the text of the letter which has been received from Professor Remigius Fresenius, acknowledging the address recently presented to him by the Society:—

"Wiesbaden, den 6ten Januar, 1895.

"An den Vorstand der Chemical Society of London.

"Sie haben mir durch Übersendung des prachtvollen Diploms, welches mir in Erinnerung bringt, dass ich seit 50 Jahren die Ehre habe Mitglied Ihrer hochangesehenen und hochachtbaren Gesellschaft zu sein, eine grosse Freude bereitet. Das Diplom, am 24ten December des verflossenen Jahres abegesandt, wurde mir am 28ten December, als an meinem 76ten Geburtsfeste, überreicht. Gestatten Sie, das ich Ihnen für die mir gewordene Auszeichnung meinen herzlichsten Dank sage.

"Wenn man auf die 50 Jahre zurückschaut, welche zwischen meinem Aufenthalt im Liebig'schen Laboratorium in Giessen und der Gegenwart liegen, und die ausserordentlichen Fortschritte in's Auge fasst, welche die Chemie in allen ihren Gebieten und welche im Zusammenhange damit die chemische Industrie gemacht hat, so kann man diess nur mit Stolz und grosser Freude thun, denn Zeiten grösseren Aufschwungs hat keine andere Wissenschaft zu verzeichnen, und wenn man sich vergegenwärtigt, dass dieser Aufsschwung dem Zusammenwirken der Forscher der verschiedenen Culturvölker zu verdanken ist, so gereicht diess zu besonderer Genugthuung. Ist es doch in Wahrheit eine Freude sagen zu können, es gibt noch Gebiete, auf denen die Nationen sich nicht bekämpfen, sondern auf denen sie sich zur Förderung gemeinsamer Interessen und zur Errechnung gemeinsamer Ziele freundlich die Hände reichen.

"Es war mir vergönnt an der Lösung der Aufgaben der Chemie 5 Decennien hindurch mitwirken zu können und ch freue mich dessen von ganzem Herzen, und wenn ich auch jetzt den Fortschritten der Wissenschaft nicht mehr in allen ihren Theilen zu folgen vermag, so bin ich doch aufrichtigen Dankes voll, dass mir immer noch Lust, Liebe und auch eine gewisse Kraft geblieben ist in meinem 77ten Lebensjahre an der Förderung der analytischen Chemie mitarbeiten zu können.

"Ihr schönes Diplom schliesst mit dem freundlichen Wunsche, dass mir diese Mitarbeit noch langere Zeit vergönnt sein möge und verpflichtet mich heirdurch noch zu ganz besonderem Dank.

"Ich wünsche der Chemical Society stets Wachsen und Gedeihen und bitte meiner auch fernerhin freundlich zu gedenken.

"Mit vorzüglicher Hochachtung,

"C. R. FRESENIUS."

Of the following papers those marked * were read:—

*1. "*Octacetylmaltose.*" By ARTHUR R. LING and JULIAN L. BAKER.

Octacetylmaltose, $C_{12}H_{14}(OC_2H_3O)_8O_3$, is obtained by boiling maltose with acetic anhydride and anhydrous sodium acetate (Liebermann's method). It crystallises from alcohol in magnificent long prismatic needles, melts at 158—159° without decomposing, is sparingly soluble in cold alcohol, readily so in benzene, glacial acetic acid, and hot alcohol, and extremely soluble in chloroform, but insoluble in water. Its specific rotatory power in chloroform is $[\alpha]_D = +62\cdot22$ (mean of two observations), and in alcohol (two observations) $[\alpha]_D = +59\cdot31$. No birotation was observed. The compound has no taste. Herzfeld (*Ber.*, xiii., 267; *Annalen*, ccxx., 215) has described an octacetylmaltose, prepared by the same method. He states that it crystallises from alcohol in colourless prisms, melting at 150—155°, but decomposing, that it has a bitter taste, is insoluble in chloroform, and has a specific rotatory power in alcohol $[\alpha]_D + 81\cdot8$. The authors, therefore, conclude that Herzfeld's description of the compound is in many respects erroneous.

*2. "*Action of Diastase on Starch.*" By ARTHUR R. LING and JULIAN L. BAKER.

The authors have carried out numerous experiments in order to prove the existence or otherwise of Lintner's so-called isomaltose, which is said to be one of the products of the hydrolysis of starch (*Ber.*, xxvi., 2538). As the result of a study of the action of precipitated diastase (prepared from low-dried distillers' malt by Lintner's method) on starch, they have isolated a very hygroscopic substance having, roughly speaking, the same properties as Lintner's supposed compound, thus: $[\alpha]_D$ 143, and R (= per cent of maltose) = 81·5. This substance gave numbers on analysis agreeing with the formula $C_{12}H_{22}O_{11}$, and cryoscopic determinations seemed to point to this as the molecular formula. A microscopic examination of the substance showed, however, that it contained crystals resembling maltose, and it yielded nearly half its weight of octacetylmaltose on acetylation. Treated with diastase, the reducing-power was raised to $R = 94\cdot6$, but the sp. gr. of the solution before and after treatment remained unaltered, a point to which Hiepe has drawn attention. It was found to ferment but slowly with ordinary beer yeast, the unfermented residue being unaltered in properties. The osazone was separable into a large fraction melting at 182—185° which resembled maltosazone in appearance, and a very small fraction melting at 145—152°. The authors suggest tentatively, that the substance may possibly contain the simple dextrin $C_{12}H_{20}O_{10} + H_2O$, a view which derives some support from the fact that the sp. gr. of a solution remains unaltered after being submitted to the action of diastase.

When starch paste is treated at 70° with the diastase obtained from pale brewers' malt, which is dried at a much higher temperature than that manufactured for distillers, the alcoholic extract of the product yields, on treatment with phenylhydrazine, a small quantity of glucosazone, and an osazone which, when repeatedly recrystallised from hot water, has all the properties of Lintner's so-called isomaltosazone; thus, it crystallises in nodular groups of extremely minute yellow needles, and melts at 150—153°. On analysing this substance, it gave the numbers of a *triosazone*. The mean analytical values are found: $C = 52\cdot73$; $H = 6\cdot20$; $N = 8\cdot31$ per cent. The formula $C_{12}H_{20}O_9(N_2HC_6H_5)_2$ requires $C = 52\cdot78$; $H = 6\cdot15$; $N = 8\cdot21$ per cent.

The authors therefore are inclined to conclude that a triose, $C_{18}H_{32}O_{16}$, is one of the products of the action of diastase on starch, and are now attempting its isolation.

Discussion.

Mr. Horace T. Brown expressed satisfaction that the question of the hydrolysis of starch was once more attracting the attention of English chemists. The authors' recent work promised to be a valuable contribution to the subject. As the speaker and Dr. Morris are at the present time engaged in a thorough re-investition of the chemistry of starch hydrolysis, he could not say much about it on this occasion, but hoped to lay their results before the society at no far distant date.

It was satisfactory that the authors had been able to confirm the existence of the maltodextrin described by Dr. Morris and himself. It has recently been urged by Lintner that this is not a pure substance, but a mixture of his "isomaltose" with the dextrins; such, however, is not the fact. Whilst admitting that every credit is due to C. J. Lintner for first calling attention to the fact that amongst the products of starch hydrolysis there is a substance other than maltose, producing a definite and crystallisable osazone, there was no doubt in the speaker's mind that Lintner was mistaken both as to the constitution and properties of the substance in question, and he agreed so far with the authors that Lintner's isomaltose was not a chemical entity. He was not prepared, however to admit the triose nature of the substance yielding the osazone described, and could not regard the mere analysis of the osazone as a proof of this.

*3. "*New Derivatives from α-Dibromocamphor.*" By Martin O. Forster, Ph.D.

Among the many well-known peculiarities displayed by derivatives of camphor, is the fact that whilst monobromocamphor is readily acted on by somewhat dilute nitric acid, being in part converted into a nitro-derivative and in part oxidised to camphoric acid, α-dibromocamphor (m. p. 61°) is unaltered by acid of the strength which at once attacks the mono-derivative, although its conversion into monobromocamphor is readily effected by digestion with alcoholic potash. At Dr. Armstrong's suggestion the author has extended the study of dibromocamphor in the hope of explaining its relationship with monobromocamphor, and at the same time of throwing further light on the nature of camphor itself. The experiments form part of a comprehensive series now being carried on in the Central Technical College Laboratory with the object of investigating the behaviour of the substituted derivatives of camphor generally.

Whereas dilute nitric acid is without action on α-dibromocamphor, spontaneous development of heat is observed to attend its dissolution in the fuming acid (d. 1·52), the action culminating at about 70° in brisk evolution of red fumes. The chief product is a colourless solid, which crystallises from alcohol in long, prismatic needles melting at 152°. On analysis this has given the following results:—Carbon 36·86 and 36·95; hydrogen, 4·38 and 4·36; bromine, 49·13, 49·50, and 49·20, the values calculated for the formula $C_{10}H_{12}Br_2O_2$, being 37·03 carbon, 3·70 hydrogen, and 49·38 bromine, it seems probable that by the action of nitric acid two atoms of hydrogen in dibromocamphor are displaced by an atom of oxygen. The substance is neutral in character, and does not appear to be acted on either by phenylhydrazine or by hydroxylamine; hot sodium ethoxide converts it into a substance soluble in alkalis, which does not contain bromine.

When the solution of the new derivative in hot alcohol is digested with zinc dust and ammonia it is reduced. The product crystallises in thin, lustrous, hexagonal plates melting at 159°. On analysis it is found to contain 48·81 carbon, 6·08 hydrogen, 32·44 bromine; the values calculated for $C_{10}H_{13}BrO_2$ being 48·98 carbon, 5·30 hydrogen, 32 65 bromine. The compound has phenolic properties, and forms a dark green, crystalline copper salt, but remains unchanged when heated on the water bath with acetic anhydride and sodium acetate. Sodium ethoxide has no action on it; on treatment with bromine it is re-converted into the original dibromo-compound (m. p. 152°).

On adding fuming nitric acid to the solution of the monobromo-derivative in glacial acetic acid, the liquid acquires a green colour, and on warming it a violent action is set up, red fumes being evolved. In this way a nitro-derivative is obtained crystallising in colourless needles which melt at 125°, containing carbon, 40·82; hydrogen, 4·82; bromine, 29·70; nitrogen, 5·56. The values calculated for $C_9H_{12}BrO{\cdot}NO_2$ being 41·22 carbon, 4·58 hydrogen, 30·53 bromine, and 5·34 nitrogen, it appears that, simultaneously with nitration, elimination of a carbonyl group has taken place, a change which is in some respects comparable with the formation of sulphocamphylic acid from camphoric acid. When this nitro-compound is reduced in alcoholic solution with zinc dust and ammonia, bromine is eliminated, and a colourless nitrogenous substance is formed, crystallising from boiling water in lustrous laminæ which melt at 159—162°.

A remarkable feature of the change undergone by α-dibromocamphor in contact with fuming nitric acid, is the formation of a small quantity of ordinary monobromocamphor melting at 76°.

It is proposed to study the behaviour of other camphor derivatives, especially bromochlorocamphor and dichlorocamphor, towards nitric acid. From the former a new substance has already been obtained, together with monobromocamphor. The new product crystallises in fine silky needles melting at 143·5°; on reduction it yields a phenolic, monohaloïd derivative from which it may be reproduced by bromination. The description of these compounds is reserved for a later communication, together with the products of the sulphonation of α-dibromocamphor, which, it is found, may be effected without difficulty.

*4. "*Acid Sulphate of Hydroxylamine.*" By E. Divers, M.D., F.R.S.

The author has prepared crystalline hydroxylamine hydrogen sulphate, NH_2OH,H_2SO_4, by acting on solid hydroxylamine hydrochloride with the calculated quantity of sulphuric acid. When the first action is over, the product is heated during several hours at 100° to expel hydrogen chloride, and the cold viscid liquid left in a desiccator until it has set to a translucent mass of prismatic crystals. These, after drying on a porous tile, were analysed, and furnished results agreeing with those calculated from the formula.

*5. "*The Hypophosphites of Mercury and Bismuth.*" By S. Hada.

Attempts to prepare a mercurous hypophosphite were unsuccessful. By acting on a solution of mercuric or mercurous nitrate with potassium hypophosphite, a white, unstable precipitate of the double mercurous nitrate and hypophosphite, $HgH_2PO_2,HgNO_3,H_2O$, is obtained. This salt explodes when heated above 100°.

Bismuth Hypophosphite, $Bi(H_2PO_2)_3,H_2O$, is readily prepared by adding a solution of bismuth nitrate to a solution of potassium hypophosphite. It is a white, crystalline powder, which is fairly stable when dry. When strongly heated, this salt decomposes in accordance with the equation $3Bi(H_2PO_2)_3 = 2Bi + Bi(PO_3)_3 + 6P + 9H_2O$.

6. "*Kamala.*" Part II. By A. G. Perkin.

The three acids melting respectively at 282°, 226°, and 232°, produced by the action of nitric acid on rottlerine (*Trans.* 1893, 982), have been prepared in larger quantity and re-examined, with the result that they were found to contain nitrogen, and to consist of *ortho-* and *paranitrocinnamic* acids and *paranitrobenzoic acid. Paranitrobenzaldehyde* was also isolated from among the products of this action. Paranitrobenzoic acid, also obtained in a similar way from the resins of high and low melting points and isorottlerine (*Trans.*, 1893, 986, 989, 990), results evidently from the oxidation of the paranitrocinnamic acid which is first formed.

Crystalline metallic compounds of rottlerine have been prepared, having respectively the formulæ $C_{33}H_{29}O_9Na$, $C_{33}H_{29}O_9K$, $(C_{33}H_{29}O_9)_2Ba$, $(C_{33}H_{29}O_9)_2Pb$, and $C_{33}H_{29}O_9Ag$, showing that rottlerine must be represented as $C_{33}H_{30}O_9$, or three times the formula $C_{11}H_{10}O_3$ originally assigned to it by Anderson (*Edin. New. Phil. J.*, i., 300). These results point also to the probability that rottlerine is a monobasic acid, $C_{32}H_{29}O_7.COOH$.

When boiled with sodium carbonate solution rottlerine is decomposed, yielding, together with resinous products, a substance crystallising in garnet-coloured prisms, to which the formula $C_{29}H_{26}O_6$ has been provisionally assigned. It is insoluble in aqueous alkalis, except in presence of alcohol. For this substance the name *rottlerone* is proposed.

7. "*The Action of Aqueous Potassium Cyanide on Gold and Silver in presence of Oxygen.*" By J. S. MACLAURIN, B.Sc., University College, Auckland, New Zealand.

This is a continuation of a paper (*Trans.*, 1893, 724—738) in which the interaction of gold and potassium cyanide—the basis of the now extensively applied Mac Arthur-Forrest or Cassell process—was investigated.

Further results are quoted proving the necessity of oxygen. The rate of dissolution of gold in potassium cyanide solutions is re-investigated, and that of silver is also determined. The rate of dissolution increases as the concentration of the solution decreases, reaching a maximum when solutions containing 0·25 per cent are used, and then decreasing. It is also shown that the ratio of the gold dissolved by any given cyanide solution to that of the silver dissolved by the same solution is approximately the ratio of their atomic weights. The remarkable variations in the solubility of gold and silver may be explained by the fact that the solubility of oxygen in cyanide solutions decreases as the concentration increases, and that the solvent power of the strong solutions is thus rendered less than that of the weaker solutions which are capable of taking up more oxygen. The relations of the gold, silver, and oxygen dissolved are shown in a table under headings—

$$\frac{Au}{O} \text{ and } \frac{Ag}{O},$$

and it is pointed out that if the amount of gold or silver dissolved depend solely on the quantity of oxygen in solution, the values—

$$\frac{Au}{O} \text{ and } \frac{Ag}{O}$$

should be constant; actually these values gradually decrease as the concentration of the solution increases. Therefore in the more concentrated solutions there is less metal dissolved than the amount of oxygen in solution apparently demands. This points to some retarding action on the motion of the oxygen molecules. As it seemed probable that viscosity would have such a retarding action, the rates of dissolution of gold and silver were determined in cyanide solutions rendered more viscous by the addition of various substances, such as sugar and glycerol, which might be assumed to exert no chemical influence on the solubility of these metals. The results show that the assumption is correct. Moreover, the viscosity coefficients of cyanide solutions of varying strengths were determined, and the values—

$$\frac{Au}{O} \text{ and } \frac{Ag}{O}$$

were calculated by the aid of a formula previously given; these agree very closely with those found, showing that the rates of dissolution of gold and silver are proportional to the amount of oxygen in solution, and to the coefficient of viscosity.

8. "*The Crystalline Form of the Isomeric Dimethylpimelic Acids.*" By WILLIAM J. POPE.

In order to obtain confirmatory evidence of the distinct nature of the two dimethylpimelic acids isolated by Dr. Kipping, a crystallographic examination of the two products was undertaken.

The acid melting at 81°—81·5°—paradimethylpimelic acid — crystallises on spontaneous evaporation of its aqueous solution in minute colourless rhombohedra belonging to the monosymmetric system, and showing the forms $c\ \{001\}$, $a\ \{100\}$, and $m\ \{110\}$; in one case a face of the form $p\ \{11\bar{1}\}$ was observed; $a : b : c = 1·263 : 1 : 1·062$. $\beta = 43° 23'$. It sometimes crystallises in flat rhomboidal plates showing the forms $c\ \{001\}$, $p\ \{11\bar{1}\}$, and $p'\ \{111\}$, which have the same crystalline form as the rhombohedra.

The acid melting at 76—76·5°—antidimethylpimelic acid—crystallises from its aqueous solution in small orthorhombic prisms showing the forms $m\ \{110\}$ and $p\ \{101\}$; $a : b : c = 0·821 : 1 : 2·862$. A well-defined orthorhombic interference figure of large axial angle is seen through the face p (101); the optic axial plane is parallel to b (010).

The crystallographic comparison of the two acids thus confirms their chemical dissimilarity in the most striking way.

9. "*Oxidising Action of Ammonia Solution on some Metals.*" By W. R. HODGKINSON and Lieut. N. E. BELLAIRS, R.A.

That an oxidation takes place when copper, moistened with ammonia solution, is placed in contact with air seems to be generally known (Schönbein, *Ber. Ak. B.*, 1856, 580; *J. B.*, lvi., 311; *Ann. Chim. Phys.*, [4], i., 381; Peligot, *Compt. Rend.*, xlvii., 1034).

Undoubtedly both copper and ammonia become oxidised in this case. As other metals dissolve to some extent in ammonia solution, the authors have determined whether any similar oxidation took place under ordinary conditions of temperature.

As might be expected, those metals which form soluble double salts with ammonium salts are most acted on by ammonia solution.

Zinc, nickel, and cobalt are, after copper, most rapidly attacked, a considerable amount of metal in each case being dissolved. Lead dissolves more slowly, and iron, magnesium, and aluminium do not appear to dissolve at all.

In the case of copper, the formation of nitrite is detectible after ten minutes' contact of the metal and ammonia in presence of air. To make a comparative test, the metals mentioned were exposed in small pieces to ammonia solution, and air in similar flasks covered only with watch-glasses during forty-eight hours. They were then examined for nitrite or nitrate by (1) potassium iodide, (2) ferrous sulphate, and (3) naphthylamine sulphanilic acid.

Zinc, nickel, lead, magnesium, aluminium, iron, and palladium in foil failed to form any nitrite.

The nickel was obtained from nickel carbonyl. After more than a week's exposure to the ammonia, although it formed a deep blue solution, no trace of nitrite was found. Cobalt, however, even after twelve hours, afforded a very appreciable amount of nitrite, the amount appearing to increase regularly with the time of exposure.

10. "*Action of Magnesium on some Phenylhydrazine Compounds.*" By W. R. HODGKINSON and A. H. COOTE.

In a note to the Society (*Proc.*, cxxxvii., p. 80) the authors described very shortly the action of magnesium on phenylhydrazine.

This metal acts on the acid derivatives with less violence than on phenylhydrazine itself, but it is still energetic when the magnesium is employed in the form of filings.

Acetylphenylhydrazine, $C_6H_5NHNHCOCH_3$, melting at 128°, was mixed with magnesium filings and heated somewhat quickly in a retort to a little above its boiling-point; there was considerable frothing and evolution of gases, which proved to be hydrogen and nitrogen; the water over which they were collected contained much ammonia. Other products, condensed before reaching the water, were benzene, aniline, acetanilide, and ammonium acetate, with a little unchanged acetphenylhydrazine. The retort residue contained magnesium acetate, magnesium oxide, and some carbonaceous matter.

It seems probable that the first attack of the magnesium is on some of the acetyl groups, which thus furnish hydrogen, which, in turn, splits up other molecules of the acetylphenylhydrazine into aniline, benzene, &c.

The action is, therefore, somewhat different from that of the metal on phenylhydrazine.

Acetanilide, phthalanil, and soveral other anilides can be distilled over magnesium without appreciable action or change.

Benzoylphenylhydrazine behaves like the acetyl compound. The products of the action of magnesium are hydrogen, nitrogen, ammonia, benzene, aniline, and ammonium benzoate.

So far the amounts of *benzene*, *aniline*, and *acetanilide* obtained indicate that $4(C_6H_5NHNHCOCH_3)$ gives—

$$2(C_6H_5NH_2)+C_6H_6+C_6H_5NHCOCH_3+3NH_3\ ;$$

the other products are still undetermined.

11. "*Refraction Equivalents of the Elements and the Periodic Law.*" By R. M. Deeley.

In this paper it is shown that the refraction equivalents of the elements for the most part fall into line with the modified periodic arrangement of the elements, which the author has previously suggested (*Trans.*, 1894).

PHYSICAL SOCIETY.

Ordinary Meeting, January 25th, 1895.

Mr. Medley concluded the reading of a paper by Prof. Ayrton and himself on "*Tests of Glow-Lamps,*" which was commenced at a former meeting.

With the newer lamps employed in these tests, it was found that candle power, current, and candles per watt all rose as the lives of the lamps increased. The authors, being surprised at this result, took care to satisfy themselves that the effect observed was due neither to change in the resistance of their manganin potentiometer strip, nor to uncertainty of contact at the sockets of the lamps. Starting again with new lamps, they found that in all cases the light given out was greater after the lamps had been glowing for some time than it was when they were new. In the earlier tests a considerable falling off in candle power had always taken place after the lamps had been running for some time. Further, while the globes of the earlier lamps were always much blackened, even after a run of a few hundred hours, and so became comparatively useless long before the filament broke, the Edison-Swan lamps now examined showed hardly any blackening, even when the filaments lasted over 1300 hours. The rise in candle-power was always accompanied by a rise in current, which was, however, proportionately much smaller, so that the consumption of power per candle was actually less after the lamp had been running 50 hours than it was at the beginning. Among the conclusions drawn by the authors were the following:—(*a*) When a group of Edison-Swan lamps marked 100—8 are run at 100 volts, and each lamp as its filament breaks is replaced by a new one, it may be expected that the light given out will never subsequently be as small as when all the lamps were new; (*b*) an Edison-Swan lamp marked 100—8 when run at 100 volts, will give an average illumination of about ten candles, and will absorb on an average power of about 4·3 watts per candle, so that such a lamp must be regarded as a 43-watt lamp, and not a 30-watt lamp as is frequently stated; (*c*) the maximum rise of light recorded during the life of any lamp was 45 per cent; (*d*) with lamps of the type examined, there is no point at which it becomes economical to discard a lamp before its filament actually breaks; (*e*) no marked economy can be gained by over-running such lamps (*i.e.*, by using pressures exceeding 100 volts).

Professor Ayrton mentioned that the improvement in glow-lamps after running for some time had been attributed to an improvement in the vacuum. Experiments made on new and used lamps by means of an induction coil, showed that the more a lamp was used the better the vacuum became, but he (Prof. Ayrton), though at first inclined to adopt this explanation, had since found that, though in all the lamps examined, the progressive improvement of the vacuum was equally marked, the increase in candle power varied between very wide limits, being very considerable in some lamps and hardly perceptible in others.

Professor Rücker asked if it made any difference to the life of a lamp whether it were kept running continuously until the fibre broke, or were run for periods of a few hours, alternating with intervals of rest. The latter case would more nearly correspond with the conditions obtaining in practice.

Professor Ayrton replied that the lamps were kept running during the night, and were disconnected during the day.

A paper by Prof. Anderson and Mr. J. A. McClelland "*On the Temperature of Maximum Density of Water, and its Co-efficient of Expansion in the Neighbourhood of this Temperature,*" was read by the secretary, Mr. Elder.

The dilatometer method was used, but the bulb of the instrument contained a quantity of mercury, determined by experiment, which for the range of temperature concerned was such as to secure the constancy of the remaining internal volume occupied by water. The observed changes were thus the real and not the apparent changes. The bulb was furnished with a graduated tube of small bore, bent twice at right angles, which served at the same time the purpose of a ground glass stopper. (The joint was made water-tight by a little Canada balsam). To determine the coefficient of expansion of the glass, the bulb and tube were fitted with mercury at 0° C., and heated up to about 9·7° C., the necessary weighings being afterwards performed. The coefficient of expansion of mercury being known, the number of grms. of mercury to be kept in the bulb during the experiments on water was calculated. The dilatometer was next filled with (thoroughly boiled) distilled water at about 8° C., the stopper end of the graduated tube inserted, and the free end dipped under mercury, giving at 4° C. a column of mercury whose changes of level could be observed. A thermometer was placed with its bulb close to the middle part of that of the dilatometer; both being immersed in a water-bath which could be cooled by the addition of ice-cold water, or cooled by radiation from surrounding objects. The thermometer used was graduated to tenths of a degree, and was compared with two similarly graduated ones by different makers. The two latter agreed very closely with one another, and one had a Kew certificate showing no error in the readings. Temperatures were written to the fourth decimal place, but accuracy to this extent was not claimed. Three sets of experiments were made, and for each a corresponding curve was drawn. In the first the water was at atmospheric pressure; in the other two at 1½ and 2 atmospheres respectively. Corresponding to these three pressures the temperatures of maximum density found were 4·1844° C., 4·1823°, and 4·1756°. The value 4·1844° corresponding to atmospheric pressure is greater than that generally received.

Mr. Rhodes thought that sufficient precaution had not been taken to accurately calibrate the thermometers. He doubted whether temperatures read in the manner described could be relied upon to much less than 0·1 degree. He did not see that any real advantage was gained by having mercury inside the dilatometer to compensate for the expansion of the glass.

Mr. W. **Watson** thought that the mercury within the vessel would cause further uncertainty by tending to produce distortion of the glass. He pointed out that in the case of water at maximum density, there would be practically no convection currents, so that equalisation of temperature would be very slow. As the bulb used was about 8 c.m. in diameter, and all the experiments were made with the temperature rising, he thought that this would account for the high value obtained for the temperature of maximum density.

Dr. **Burton** thought a distinct advantage was gained by compensating for the expansion of the glass. The values obtained in different experiments did not seem to be highly concordant.

Professor **Rücker** thought that the criticisms which had been passed were for the most part just. For such measurements as those recorded, it was not sufficient to know the corrections of the thermometer readings at a few isolated points; the portion of the stem over which the readings were taken must be carefully and minutely calibrated. The Kew certificate not only ignored errors of less than 0·05 degree (as mentioned by the authors), but it only gave corrections for a small number of temperatures, separated by considerable intervals.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

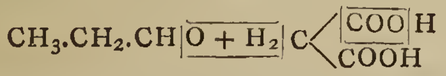
Dr. **Dobbin** in the chair.

The fifth meeting of the Society took place on the 28th January.

Dr. **Mackenzie**, of the Heriot-Watt College, read a paper on "*Unsaturated Fatty Acids.*"

By way of introduction, unsaturated acids were defined, and a short description of the nomenclature, general methods of preparation, and general properties was given. The methods of determining the constitution were more fully gone into. The method of fusion with potash was shown to give misleading results. The HBr and Br addition-products of the acids are characteristic. The $\alpha\beta$ acids give β-bromacids, which on boiling with water yield unsaturated hydrocarbons, β-oxyacids, and a mixture of $\alpha\beta$- and $\beta\gamma$-acids. $\beta\gamma$-acids give γ bromacids, which on the same treatment yield γ-lactones. Similarly $\alpha\beta$-dibromacids give monobrom unsaturated hydrocarbons besides unsaturated monobrom and monobromoxyacids. From $\beta\gamma$-dibromacids result monobrom lactones. The method of boiling with dilute sulphuric acid determines quantitatively the proportions of $\alpha\beta$- and $\beta\gamma$-acids in a mixture. The former remain unchanged, the latter yield lactones. The conversion of $\beta\gamma$ into $\alpha\beta$ and oxyacids by boiling with dilute caustic soda was noted. For a concise yet comprehensive account of the subject, members were referred to Fittig's lecture "On Unsaturated Acids" (*Ber.*, xxvii., 2658). A short account of $\alpha\beta$-pentenic acid or propylideneacetic acid, $CH_3.CH_2.CH:CH.COOH$, was then given.

Komnenos (*Ann.*, cxviii., 166) first obtained, by the condensation of propionaldehyd and malonic acid with glacial acetic acid, a liquid of the empirical formula $C_5H_8O_2$ and b.-p. 194°—198°, which did not solidify in a freezing mixture. From its formation,—



$$CH_3.CH_2.CH\boxed{O + H_2}C\begin{cases}\boxed{COO}H\\COOH\end{cases}$$

he concluded it to be propylideneacetic acid, and this remained undisputed for some years.

Zincke and Küster (*Ber.*, xxii., 486), by reduction of a pentachloracid, obtained a liquid which they found identical with that of Komnenos. This they considered to be propylideneacetic acid, although its HBr addition-product gave a lactone on boiling with water, contrary to the general behaviour of $\alpha\beta$-acids. Two years later, Ott (*Ber.*, xxiv., 2600) described the separation of the Ba salt of Komnenos' acid into a part soluble and one insoluble in alcohol. From the re-crystallised insoluble salt he prepared an acid of b.-p. 193·5°. From another fraction of the insoluble salt he prepared $\beta\gamma$-pentenic acid (ethylidenepropionic acid) of b.-p. 193—194°. Dibromides of both acids were alike in m.-p. and crystallographic properties. Two years later, Viefhaus (*Ber.*, xxvi., 915) repeated Ott's work, but came to the conclusion that acid from the Ba salt soluble in alcohol was the $\alpha\beta$-acid, and that from the insoluble salt the $\beta\gamma$ acid, because the former gave only 20 per cent, the latter 70 per cent lactone, on boiling with sulphuric acid. Evidently both acids were impure. The $\alpha\beta$-acid was at the time of Viefhaus' publication obtained pure by Fittig and Mackenzie. By partial separation by means of the Ba salt, and then boiling with sulphuric acid until no more lactone resulted, a liquid was obtained which boiled at 200°—201° without decomposition, and on cooling solidified to leafy crystals of m.-p. 9·5°—10·5°. The HBr and Br addition products were also got in crystalline form. The former yielded the products expected on boiling with water. In the same research it was found that by fractional crystallisation of the insoluble Ba salt, the $\beta\gamma$-acid was obtained pure. For further particulars members were referred to *Liebig's Annalen*, cclxxxiii, 82. In the last issue of the *Berichte* (xxvii., 3364), Zincke writes that on repeating his work, he finds the acid obtained by Küster and himself to be $\beta\gamma$-acid, and to contain no $\alpha\beta$-acid.

CORRESPONDENCE.

ARGON.

To the Editor of the Chemical News.

Sir,—In a paper recently communicated to the Chemical Society, I have shown that the refraction equivalents of the elements vary periodically with much regularity. The following tables show the nature of the variation for those elements with which argon must it seems be classed.

Element.	Atomic weight.	Refraction-equivalent
Carbon	12	5 or 6
Nitrogen	14	4·1
Oxygen	16	2·8 or 3·4
Fluorine	19	1·6
Argon	20?	?
Sodium	23	4·3
Magnesium	24·3	6·7
Aluminium	27	7·7
Or—		
Potassium	39	7·85
Calcium	40	10·0
Argon	40?	?
Scandium	44?	?
Titanium	48	24·0

From potassium to titanium the refraction-equivalent rises rapidly, the value for calcium being 10. If argon, like calcium, has an atomic weight of 40, we should expect to find its refraction-equivalent also about 10. On the other hand, if its atomic weight be 20, and it falls between fluorine and sodium, the refraction-equivalent might be 3 or even smaller than that of fluorine. For between carbon and aluminium the refraction-equivalents decrease rapidly until fluorine is reached. They then increase, with increasing atomic weight, and more than regain their original value at aluminium.

As the refraction-equivalent is calculated from—

$$P\frac{\mu-1}{d};$$

P being the atomic weight, its value will depend upon the position assigned to the element on the atomic scale. Three and ten, however, not bearing the same ratio to each other as do twenty and forty, different refractive indexes are required for the two positions.

A determination of this physical constant would enable us to calculate the refraction-equivalent of argon, and the figure so obtained might point clearly to one of the possible values, 20 or 40, being the correct atomic weight of the new element.—I am, &c.,

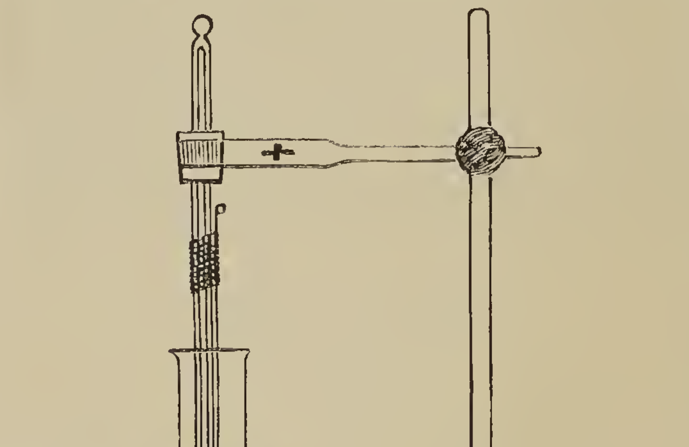
R. M. Deeley.

1, Charnwood Street, Derby,
February 2, 1895.

TAKING MELTING- AND IGNITING-POINTS.

To the Editor of the Chemical News.

Sir,—The enclosed is a rough sketch of an apparatus I have employed in my classes for some years for taking melting-points and igniting-points of explosives.



A. 2-oz. flask.
B. Test-tube.
C. Thermometer with cup.
D. Asbestos packing.

For the latter a small platinum foil cup, about 2 m.m. wide and deep, is soldered to a platinum wire and suspended, as shown, close to the thermometer bulb and free in the centre of the test-tube. The outer flask (A) stands on two thicknesses of wire gauze, and is heated through this by the Bunsen flame so that a faint blue flame plays 2 or 3 c.m. high around the flask, and the wire gauze is scarcely red hot. Igniting point results are very satisfactory; for instance, nitroglycerine, four determinations, gave 158°, 157,° 158°, 157°.—I am, &c.,

W. R. Hodgkinson.

Artillery College.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 2, January 14, 1895.

Autumn Crops.—P. P. Dehérain.—The author has from time to time drawn attention to the considerable loss of nitrates undergone in autumn by soils after the removal of their crops, and insisted on the advantages of intermediate autumn crops. He now returns to the subject, showing that fields left bare lose weights of nitrates often greater than that applied in Spring as manure. This loss represents a sum equal to the rent of the land in a great part of France. He points out that in certain districts the soil is covered with an intermediate crop sown immediately after harvest and consisting by preference of leguminous plants.

Nomination.—The Academy proceeded to nominate a member of the Section of Mineralagy *vice* M. Mallard, deceased. The successful candidate was M. Hautefeuille.

Experimental Researches on the Critical-point of Liquids Holding Solids in Solution.—Raoul Pictet.—The author attempts to determine experimentally what is the solvent power of the vapours of liquids raised to a temperature above their critical-point. He finds that camphor is gaseous, or in a gaseous solution in the vapours of ether. Borneol remained totally dissolved in gases or in the vapours of ether. Guaiacol, phenol, and iodine behaved in a similar manner. Vapours of alcohol at 240° dissolve alizarin like liquid alcohol. The liquefaction of vapours presents two distinct phases: the one at temperatures above the critical-point, in a multitude of points at the centre of the vapours, the number of which is proportional to the pressure; the other phase is below the critical-point at the pressure of saturated vapours. Solids, on the contrary, dissolve in the total of the liquid vesicles disseminated among the vapours under a high pressure near the critical-point.

Certain Properties of Silver Sulphide.—A. Ditte.

Preparation of Amorphous Silicon.—M. Vigouroux.

Protomorphic Condition.—A. Villiers.

Certain Sensitive Reactions of the Amidobenzoic Acids.—Oechsner de Coninck.—These four papers will be inserted *in extenso* as early as possible.

A Class of Nitriles.—Albert Colson.—The ethers of the cyanals resist heat, but in contrast to the cyanic ethers they easily give off the elements of hydrocyanic acid. The author is about to examine if insoluble cyanic ether is or is not connected with the cyanals.

Constitution of Hexamethylentetramine.—R. Cambier and A. Brochat.—Methylenamidoacetonitrile is to hydrocyanic acid what hexamethylenamine is to ammonia.

Ethylenic Methylal.—L. Henry.—Not adapted for useful abstraction.

New Researches on Pectase and Pectic Fermentation.—G. Bertrand and A. Mallèvre.—We may conclude from these new researches that pectase exists in the cellular juice of acid fruits as in that of the roots of carrots. There is no insoluble pectase. But in the juice of acid fruits the presence of the ferment may be masked by the acidity of the medium, and its action then appears only on neutralisation.

No. 3, January 21.

On Boron Steel.—H. Moissan and G. Charpy.—The study of a compound of iron with small proportions of boron presents much interest, both from a practical and a theoretical point of view. The analogies existing between carbon and boron, and the difference of their atomic volume, render these experiments interesting as throwing a light on the constitution of steels. The authors have prepared an ingot of iron containing—

Boron	0·580
Carbon	0·17
Manganese	0·30
Silicon, phosphorus, sulphur	traces.

This alloy was rolled into a cylindrical bar, and it is easily forged at a dark-red heat; in a general manner it works like mild steel. Boron communicates to iron the property of taking a temper, but a special temper corresponding to an increase of the breaking strain without any appreciable augmentation of hardness. Its *rôle* is therefore quite distinct from that of carbon.

Nominations.—The Academy proceeded to nominate a correspondent for the Section of Medicine and Surgery, *vice* the late M. Pollet. M. Herrgott obtained an absolute majority of votes. The Academy next appointed a Commission to draw up a list of candidates for the rank of Foreign Associate, *vice* the late Herr Kummer.

Influence of Temperature on the Transformation of Amorphous Zinc Sulphide. — A. Villiers. — The temperature of transformation is not fixed for one and the same substance. It depends on the medium in which the substance exists at the moment of its formation, and also on the conditions which this medium has subsequently undergone. The temperature is very different for different media. It may be near zero or above 100°, according to the composition of the liquid and the variations of this composition during and after the precipitation of the zinc sulphide.

Insufficiency of Kjeldahl's Method for Determining Nitrogen in the Chloroplatinates. — M. Delépine.—In determining by this method the nitrogen in trimethylamine chloroplatinate the anthor found only 3·88 of nitrogen instead of the calculated quantity of 5·15 per cent. In a specimen of ammonium chloroplatinate he observed only 1·89 per cent in place of 6·26. This deficiency seems due to the action of the chlorine of the platinum chloride upon the ammonia, and doubtless upon the amine.

Upon Arabinochloral and Xylochloral.— M. Hanriot. — The author has previously shown that glucose may combine with chloral forming two isomers, the glucochlorals. He now seeks to generalise this reaction by extending it to other sugar. Arabinochloral answers to the formula $C_7H_9Cl_3O_5$. It is slightly soluble in cold water and chloroform, fairly soluble in heat in alcohol, ether, and benzene. Its rotatory power is $[\alpha]_D = -23{\cdot}2^{\circ}$. With various reagents it behaves like β-glucochloral, though with orcine hydrochlorate it gives a blue colour. Xylochloral crystallises in laminæ fusible at 132°, being in part volatilised before fusion. It is much more soluble in water than arabinochloral. Its rotatory power is $[\alpha]_D = -13{\cdot}6^{\circ}$. With orcine hydrochlorate it gives the same blue colour as does arabinochloral.

New Synthesis of Anthracene.—M. Delacre.—The author treated benzyl trichloracetate with benzene in presence of aluminium chloride and under the influence of heat. Instead of triphenylethane he obtained exclusively anthracene, which, after a single re-crystallisation, was perfectly pure.

A Contribution to the Study of the Tartaric Ethers.—Ph. A. Guye and J. Fayollot. — The ethers derived from the ethyl or isobutyl dextro-tartrate with a simple acid radicle are characterised by positive rotatory powers, algebraically inferior to that of the non-substituted tartrate. A full exposition of the author's views is not practicable without the accompanying diagrams.

Archives Néerlandaises des Sciences Exactes et Naturelles.

Vol. xxviii., Parts 3 and 4.

Emission of Oxygen under the Influence of Light by the Chromophyllic Cellules Demonstrated by the Bacterian Method.—Th. W. Engelmann.—The principal facts established in the author's beautiful researches are:—1. The green vegetable cells have the power of emitting oxygen in the light. 2. The intensity of this emission increases within wide limits with the intensity of the illumination. 3. The emission of oxygen begins immediately with the action of light, and ceases at the moment when darkness sets in. 4. The bacteria employed (principally *Bacterium termo*) require every instant free oxygen in order to move. 5. The rapidity of their movements increases to a large extent with the tension of the oxygen. 6. If the tension of the oxygen falls below a certain value, the movements cease at once; but they are resumed as soon as the tension is again increased. 7. The direction of the movements of the locomotion of the bacteria is influenced by the distribution of the tensions of the oxygen in the drop of liquid, chimiotaxis. The bacteria accumulate where the tension is greatest. Some species, however, such as *Vibrio lineola*, *Spirillum tenue*, &c., adapted to very low tensions of oxygen, accumulate when the tension is low in consequence of a feeble illumination. The red rays of light which are preferentially absorbed by chlorophyll determine an exceptionally strong emission of oxygen. The paper is illustrated with beautifully coloured plates, designed by the author, which are in fact necessary for his results. There is also appended a valuable bibliography of the subject.

MISCELLANEOUS.

The Name "Argon."—A valued correspondent sends us the following remarks on the origin of the name Argon:—"The root 'arg' in the name now appropriated to the new element has been employed before in a similar sense in the classification of molecules in steam into argules and ergules in Mr. Macfarlane Gray's paper on the 'Rationalisation of Regnault's Experiments on Steam.' It may be interesting to refer to the words of Jesus Christ, from which 'argule' was derived, 'Why stand ye here all day argoil.' It is this word 'idle' which appears again in the new name Argon, and the words of Jesus Christ are just what every chemist is to-day saying in regard to the new substance. The *Daily Telegraph*, in an able article on the new element, falls into a very amusing error. After remarking on the quietness of nitrogen in the atmosphere, it says 'Gentle nitrogen prevents all this; but try it in nitroglycerine, and how different its behaviour!' not knowing that it plays the same *rôle* in nitroglycerine as in the atmosphere. Nitrogen keeps the oxygen off the hydrogen and the carbon in nitroglycerine, and it is not until its pacific efforts have been overpowered by a surrounding disturbance, and when it has ceased to be nitroglycerine, that explosion occurs. In the explosion, however, the nitrogen merely walks off as if regretting that its efforts have been at last frustrated, and that these elements it had been keeping apart have in spite of it got foul of each other."

NOTES AND QUERIES.

⁎⁎ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Bichromates.—A correspondent asks for references to the best information on the manufacture of bichromates of potash and soda.

Purification of Water for Steam Boilers.—A correspondent asks where he can find detailed information on the subject of water purification, especially in relation to steam boilers.

MEETINGS FOR THE WEEK.

Monday, 11th.—Society of Arts, 4. (Cantor Lectures). "Means for Verifying Ancient Embroideries and Laces," by Alan S. Cole.
— Medical, 8.30.
Tuesday, 12th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Medical and Chirurgical, 8.30.
— Institute of Civil Engineers, 8.
— Photographic, 8. (Anniversary).
Wednesday, 13th.—Society of Arts, 8. "Light Railways," by W. M, Acworth.
— Pharmaceutical, 8.30.
Thursday, 14th.—Royal, 4.30.
— Society of Arts, 4.30. "Village Communities in Southern India," by C. Krishna Menon.
— Royal Institution, 3. "Meteorites," by L. Fletcher, M.A., F.R.S.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
Friday, 15th.—Royal Institution, 9. "Mountaineering," by Clinton T. Dent, F R.C.S.
— Geological, 3. (Anniversary).
— Quekett Club, 8. (Anniversary).
Saturday, 16th.—Royal Institution, 3. "English Country Songs" (with musical illustrations), by Sir Alexander Campbell Mackenzie, Mus. Doc.

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THE CHEMICAL NEWS.

VOL. LXXI. No. 1838.

SOME REMARKS ON "ARGON."

By BOHUSLAV BRAUNER, Ph.D.

I have read with great interest the contents of your "Argon" number of the Chemical News (vol. lxxi., p. 51), which has just reached me, and which contains the results of the classical researches of Lord Rayleigh and Professor Ramsay, Crookes, and Olszewski on that new gaseous constituent of our atmosphere.

When about two years ago I read for the first time the result of the work of Lord Rayleigh, who found that "chemical" nitrogen has a smaller density than "atmospheric" nitrogen, it struck me that this interesting fact might be explained by assuming that either "chemical" nitrogen consisted to a small extent of molecules dissociated into atoms, or that "atmospheric" nitrogen consisted partly of larger groups of atoms, *i.e.*, contained a polymeric form of nitrogen. If we compare the "volume weights" of (*a*) "chemical" nitrogen, (*b*) "normal" nitrogen, as calculated from its atomic weight, and (*c*) "atmospheric" nitrogen, we have—

$$a : b : c = 13·995 : 14·045 : 14·067,$$

and it is seen that both hypotheses may be true at the same time.

We must consider that "chemical" nitrogen has been only a short time ago liberated all in free atoms, and these nearly completely united to molecules, so that it contains for 996·5 molecules N_2 *seven atoms N*, as calculated from the above numbers.

On the other hand, "atmospheric" nitrogen is as old as creation, and in this long time not only the originally free atoms might have completely united to molecules, but by some unknown reason larger atomic complexes might have been formed.

I was therefore surprised to find that in the paper read and in the following discussion the hypothesis, brought out originally by Dewar, *i.e.*, that "argon" is a kind of "nitrogen-ozone," a larger group of nitrogen atoms, N_3, was neither mentioned nor discussed, for it is striking that the density of such a gas would be exactly $d = 21$, whereas the highest value found by Rayleigh and Ramsay is $d = 20·3$. There is a very powerful argument which speaks against the assumption that the gas is N_3, *i.e.*, the ratio of the specific heats at constant pressure to that at constant volume. I do not know whether this argument is so absolutely decisive as to make thoroughly useless any research in the direction whether the gas may still not be N_3.

Mendeleeff has shown that elements possessing a large atomic volume (in the solid state) combine easily with others, and explains this fact by assuming a comparatively large distance between the single atoms in the molecule (*e.g.*, Cs, vol. = 70), whereas elements which do not combine easily have a small atomic volume, *i.e.*, the atoms are very near each other (*e.g.*, the platinum metals, vol. = 8·3—9·2).

Though "argon" is a gas, a similar assumption of atoms lying very close to each other in the molecule would explain its great inertia, and such a close complex of three nitrogen atoms, weighing only 42, and showing no internal work, might be assumed to behave *physically* like a single atom.

The discoverers have tried several ways to induce chemical combination of argon, but as the gas seems to have been formed under conditions where other bodies decompose, it is very improbable that it will combine with other bodies under such conditions, and in fact it resists high temperatures and takes no part in reactions which are very energetic.

We have another source of powerful energy, viz., micro-organisms. We know micro-organisms which produce hydrogen arsenide from arsenic oxides; other micro-organisms convert ammonia into nitric acid, and some chemists think that they assimilate free nitrogen from the atmosphere; and last, not least, we know micro-organisms which reduce sodium carbonate to carbon monoxide. Is it not possible that such a source might have some action upon "argon"?

The most powerful source of chemical energy which is of a similar fermentative nature is nascent hydrogen liberated on contact of metallic palladium, or better rhodium, with formic acid. This thought was suggested to me by my friend Professor Rayman, who has been working in similar directions. If argon consist of polymeric nitrogen, it is probable that upon dropping formic acid upon rhodium in an atmosphere of argon, substances of the nature of hydrogen might be formed.

As an orthodox Mendeleeffian, I find great difficulty in assuming the existence of a new elementary gas having the atomic weight 20 or 40 or 80, its boiling-point being −187°. This low boiling-point would better correspond with a gas similar in its nature to nitrogen. On comparing, however, the boiling-points of O_2 and O_3 with that of N_2 and A, we find—

O_2 .. −182·7° O_3 .. −106° ($d = 76·7°$)

whereas—

N_2 .. −194·4° A .. −137° ($d = 7·4°$)

The difference between the boiling-point of oxygen and ozone is 76·7°, whereas that between nitrogen and argon is only 7·4° (*i.e.*, only the tenth of the former, so that in this case we have not the expected analogy).*

Again, the density of argon in the liquid state is about 1·5. The atomic volume,—

$$\frac{20}{1·5} = 13·3 \qquad \frac{40}{1·5} = 26·6,$$

and it is interesting to see that both these numbers find their place on the well known Lothar Meyer's curve of atomic volumes (ascending parts), *i.e.*, the atomic volumes agree well with the values expected for elements having the atomic weights either 20 or 40, and lying either between F = 19 and Na = 23, or between Cl = 35·5 and K = 39·1.

On reading very carefully the account of the discovery and the properties of argon one is struck by its great relation with nitrogen, and, in fact, the only observation which speaks against the assumption of an allotropic form of that element is of a purely physical character. We must not forget that it is contained in air to the amount of about one per cent, and that it therefore most probably plays an important *rôle* in nature and in life. We breathe 1 c.c. of argon for every 21 c.c. of oxygen, and I think that such a quantity of any other other substance but allotropic nitrogen would be hardly indifferent to our life.

Bohemian University, Prague,
February 6, 1895.

Solution of Solids in Vapours.—P. Villard.—The author states that the results obtained by Raoul Pictet (*C. R.*, Jan. 14, 1895) present a close agreement with his own relating to iodine dissolved in carbonic anhydride (*Journal de Physique*, Series 3, vol. iii., Oct., 1891). He adds that the absorption spectra in his observations, whether of the liquid or the vapour, presented in no case the flutings characteristic of gaseous iodine. Hence the latter seemed to be in a state of true solution in the vapour, even if not saturated.—*Compt. Rend.*, cxx., No. 4.

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* This want of analogy is not surprising on considering that the constitution of N_3 would very much differ from that of O_3, the latter being an endothermic very active substance. That the group N_3 *is* really differently constituted from O_3, is seen in the case of azoimide, N_3H, whereas we do not know any O_3H.

THE NASCENT STATE.

By LAUNCELOT ANDREWS, Ph.D.

I.

Mr. Joshua C. Gregory, in a recent number of the Chemical News (lxx., p. 188), criticises my previously published views on the nascent state as being too sweeping, and finds that I have "not succeeded in disproving nascent action." *That* I am quite ready to admit. All I hope to do is to show the inadequacy and the unnecessary character of the theory in a certain number of typical cases which have hitherto constituted the basis upon which the theory rested, and Mr. Gregory's objections give me a desired opportunity to record new observations bearing upon the disputed point.

He says "How else can the bleaching action of chlorine be explained? We know that moisture is necessary for this; we know that the action of chlorine is to set free oxygen; and we know, further, that this latter oxidises the colouring matter." Surely here is a sad confusion of knowledge with hypothesis!

What are the real facts with regard to the action of chlorine upon vegetable colouring matter. A solution of, say, indigo sulphuric acid in water is readily bleached by chlorine, while a piece of paper stained with the same solution, and then thoroughly dried, will withstand the action of the dried gas for a long time without visible change. This is the familiar experiment which, perhaps, Mr. Gregory had in mind in making the rather sweeping statement quoted, and which, in fact, has usually been interpreted as he interprets it.

Why is it not simpler to assume that the chlorine destroys the colouring matter by combining with its hydrogen to form hydrochloric acid gas? Two reasonable explanations can be given of the fact that the action takes place far more readily and quickly when the indigo is dissolved in water than when it is in the dry and solid form. These are—1st, the energy set free by the solution of the hydrochloric acid in the water goes to maintain the reaction (Berthelot's principle); 2nd, the failure to bleach in the second case may be due to the indigo being in the solid state, in which condition, as is well known, all reactions take place more slowly. Thus each particle of the colouring matter may well be supposed to soon become coated, in the absence of a solvent, with its own decomposition products, and so protected against further access of chlorine.

In order to test the admissibility of the second explanation, it is only necessary to dissolve indigo in a dry solvent free from oxygen, and to treat the solution with dry chlorine. If, under these conditions, the blue colour is not destroyed, the explanation just given must be faulty; but, on the other hand, if bleaching occurs, the explanation of Mr. Gregory, and with it the applicability of the nascent state hypothesis to this phenomenon, must be abandoned.

Experiment 1.—The attempt was made at first to dry a solution of indigo in chloroform with phosphoric anhydride, but this failed because the indigo gradually left the solution to combine with the phosphoric anhydride, the former becoming colourless. It was therefore necessary to dry the materials separately.

A small quantity of pure indigotin was exposed for a week in a desiccator charged freshly with phosphoric anhydride (P_2O_5). At the same time chloroform was dried by standing in contact with a quantity of the same material, the action being aided by occasional shaking. The chloroform was poured off into a well-stoppered bottle, the indigotin added, and a saturated solution of the latter in the former prepared by digestion. Some of the clear solution was then removed, and to it was added a dilute solution of bromine in chloroform which had been dried over P_2O_5 as described. Prompt bleaching ensued, the action being apparently no less rapid than in aqueous solutions.

Experiment 2.—Some of the solution of indigotin in chloroform, which had been dried as described, was treated with chlorine gas which had first passed a calcium chloride tower and then a phosphoric anhydride tube. The solution was very rapidly bleached.

From these experiments the only conclusion to be drawn is that, contrary to the general belief and to Mr. Gregory's explicit statement, *the presence of moisture is not a necessary condition to the bleaching of organic colouring matters by the halogens.* Probably the presence of *any* solvent for either the chlorine or the indigo would suffice.

II.

The reactions in which nitric acid is reduced to ammonia by the metals are exceedingly complex. It is therefore difficult to prove directly exactly what the steps are which do take place. Therefore many will doubtless prefer to adhere to the "nascent state explanation" until further investigation elucidates every step. For my part, it does not seem scientific to assume that nascent hydrogen is the active agent in the production of ammonia from nitric acid by the action of tin and hydrochloric acid, when it is a fact that stannous chloride alone is capable of quantitatively reducing nitric acid to ammonia,* the presence of nascent hydrogen being in the latter case impossible.

It would rather seem more logical to admit that, if in *any* case nitric acid can be reduced to ammonia without the presence of nascent hydrogen, the assumption of the latter as efficient cause of the reduction is needless in *all*. In order to gain further insight into the production of ammonia from oxidised compounds of nitrogen by reactions in which no hydrogen is set free, the following experiments were tried.

Experiment 3.—Crystallised stannous chloride (5 grms.) was dissolved in a large excess of a 20 per cent solution of sodium hydrate, and pure potassium nitrate (3 grms.) was dissolved in another portion of the same solvent. Both solutions were boiled in flasks provided with condensers, until the distillate no longer gave a reaction with Nessler's reagent; ammonia free distilled water, specially prepared for the purpose, being added from time to time to keep the bulk of the liquid from being too much diminished. Then the liquids were mixed and the distillation continued. The distillate, on Nesslerisation, showed no trace of ammonia.

Hence, nitrates are not reduced to ammonia by stannous hydrate in the presence of a large excess of caustic soda. This result was a surprise to me, although it should not have been, in view of the well-known great stability of the alkali nitrates at moderate temperatures. It was then argued that the less stable nitrates would be more likely to suffer reduction.

Experiment 4.—This experiment was conducted exactly like the last, except that one-tenth of a grm. of sodium nitrite was substituted for the same amount of potassium nitrate. The alkaline solutions of the nitrite and of the stannous hydrate, having been freed from every trace of ammonia, as described above, on being mixed and boiled evolved ammonia abundantly, the reduction being apparently quantitative.†

We see, therefore, that ammonia may be formed from nitric acid in acid solution by the reducing action of $SnCl_2$, and from nitrites in alkaline solution by $Sn(OH)_2$. In both cases there is no room for the assumption of nascent hydrogen, and the logical conclusion is that some explanation not involving this hypothesis and broad enough to cover all cases may and must be found. I do not think that there is at present quite enough foundation in known fact to build any theory upon, except in a suggestive and merely tentative way. In this spirit it may

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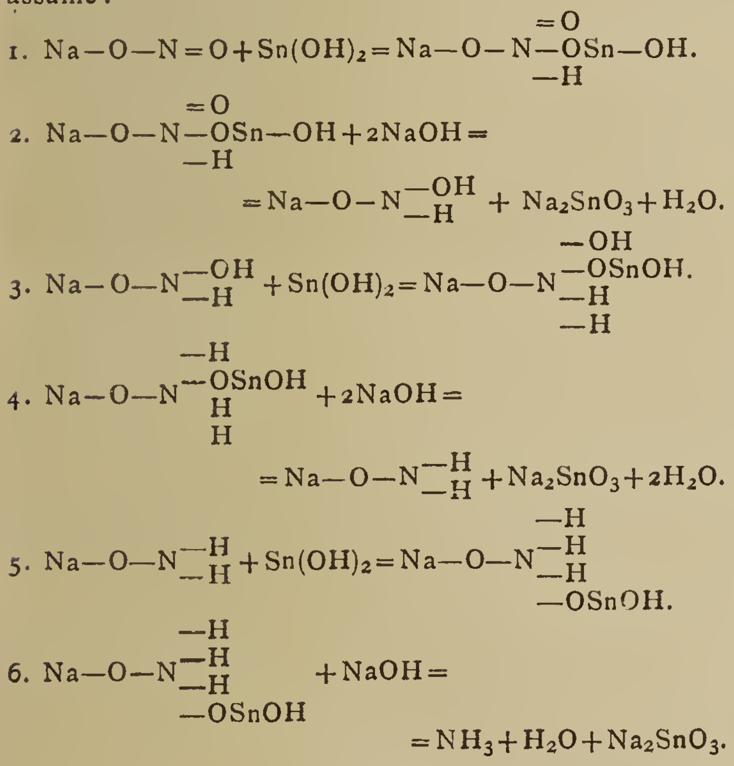
* Pugh, *Chem. Soc. Quarterly Journal*, xii, 35, abstract in *Jahresberichte*, 1859, 672.

† It is thought possible that a quantitative method for the separation of nitrites from nitrates, and for the determination of the former, can be based upon this reaction.

not be premature to point out that an analogy appears to exist between the so-called catalytic action, on the one hand, of aluminium chloride in inducing many organic syntheses, or of ferric chloride in promoting the formation of many chlorination or bromination products of organic compounds, and, on the other hand, of certain metals and of their salts in favouring the formation of ammonia from nitrous and nitric acids, and of sodium in forming highly hydrogenated products in presence of water or the alcohols.

In all these cases we have to assume the first step to consist in the formation of an addition product, the second in a reaction, of ordinary metathetic character, between the addition compound and one of the other bodies present. Such has been proved to be the true explanation of the remarkable activity of aluminium chloride. Such is probably accepted by most chemists already as the best explanation of the catalytic action of ferric chloride, and I would simply extend the explanation to cover all cases of so-called nascent action. For example, the reduction of the naphthylamines to dianoltetrahydronaphthylamines by sodium in the presence of boiling amyl alcohol would be conceived in accordance with the theory to consist in the formation of sodionaphthylamines, and in a subsequent reaction between these and the amyl alcohol, producing sodium amylate and hydronaphthylamines. Just what the addition products are, which this theory supposes to exist (for a brief moment), we cannot say, and most of them will probably defy efforts at isolation in consequence of their essentially evanescent and unstable character; but others we may well hope to discover, if we will only look for them. The close analogy of many are already known and isolated.

It may not be without interest to point out the application of this theory to the explanation of the reduction of sodium nitrite by means of stannous hydrate. We would assume:—



1. $Na-O-N=O+Sn(OH)_2=Na-O-\underset{-H}{\overset{=O}{N}}-OSn-OH.$

2. $Na-O-\underset{-H}{\overset{=O}{N}}-OSn-OH+2NaOH=$

$=Na-O-N\begin{smallmatrix}-OH\\-H\end{smallmatrix}+Na_2SnO_3+H_2O.$

3. $Na-O-N\begin{smallmatrix}-OH\\-H\end{smallmatrix}+Sn(OH)_2=Na-O-N\begin{smallmatrix}-OH\\-OSnOH.\\-H\\-H\end{smallmatrix}$

4. $Na-O-N\begin{smallmatrix}-H\\-OSnOH\\H\\H\end{smallmatrix}+2NaOH=$

$=Na-O-N\begin{smallmatrix}-H\\-H\end{smallmatrix}+Na_2SnO_3+2H_2O.$

5. $Na-O-N\begin{smallmatrix}-H\\-H\end{smallmatrix}+Sn(OH)_2=Na-O-N\begin{smallmatrix}-H\\-H\\-H\\-OSnOH.\end{smallmatrix}$

6. $Na-O-N\begin{smallmatrix}-H\\-H\\-H\\-OSnOH\end{smallmatrix}+NaOH=$

$=NH_3+H_2O+Na_2SnO_3.$

Of course, two equations instead of six would have been sufficient to make clear the leading idea, but I have preferred to employ the more complicated form because it is clearer to the mind, also because it better illustrates the progressive character of the reduction, and shows the intermediate products to be expected, any one of which may perhaps be isolated.

In concluding, I must not fail to point out that the view of Professor Smithells, which Mr. Gregory cites, stands in no necessary relation with the hypothesis of a nascent state, and many will be held as true even if the latter be discarded. It is undoubtedly true that it is often desirable to express in two equations a reaction which in fact takes place only in one stage. The value of a theory lies chiefly in its fruitfulness or in the power of prediction which it gives. The nascent state hypothesis could never have predicted the formation of ammonia from sodium nitrite by stannous hydrate, a prediction which constitutes the first fruit of the addition theory.

State University of Iowa,
Chemical Laboratory, January 18, 1895.

ON THE ACTION OF REDUCING AGENTS ON NICKELO-POTASSIC CYANIDE. MAGNETIC OXIDE OF NICKEL.

By THOMAS MOORE.

A continuation of the experiments (Chemical News, lxvii., p. 295) on this subject showed that the red solution could be produced by other means than by sodium amalgam; for example, zinc with a coating of either silver or copper acts very powerfully; it is also produced when a solution of the double cyanide containing an excess of alkali is electrolysed, the cathode being mercury. Many attempts were made to isolate the precipitate which the red solution gives with hydrochloric acid, but without success, as it rapidly decomposes whilst drying, with evolution of hydrogen. It is equally useless to try to obtain the oxide by the addition of oxycyanide of mercury, as instant decomposition takes place into metallic mercury and green oxide of nickel.

On considering what might be the action of potassium on the double cyanide, it was evident that, should a lower cyanide be actually formed, a certain amount of potassic cyanide should be set free, according to the eqnation—

$$3(NiCy_2 2KCy)+4K=Ni_3Cy_2+10KCy.$$

Now it had been already noticed that solutions containing an excess of free KCy were the least suitable for the production of the red colour. It was therefore supposed that if this free KCy could be removed the stability might be increased. This end was attained by the further addition of nickel sulphate to the solution under reduction, this forming another portion of $NiCy_2 2KCy$, which in its turn would be reduced with the formation of free cyanide. The operation is thus progressive. By proceeding in this manner more concentrated solutions can be obtained, but care must be exercised that the reduction is not pushed too far, as at a certain point the mercury commences to swell up after the manner of the ammonium amalgam, and the solution is rendered impure with little floating globules of mercury. There still remained, however, the task of precipitating the oxide, the isolation of the cyanide having been found to be surrounded by too many difficulties. This was accomplished by simply boiling the red liquor with ammonic chloride, and in this way getting rid of all cyanogen as volatile ammonic cyanide.

On boiling the properly prepared solution (that is, one containing little or no free KCy) with ammonic chloride in a non-oxidising atmosphere, a black precipitate is formed. This is washed several times by decantation, first with hot water and then with boiling dilute ammonia to which a little ammonic chloride has been added. This is repeated until the washings are free from nickel. Finally the precipitate is freed from ammonic chloride by repeated treatment with distilled water. By this means the precipitate is freed from all cyanide and oxide of nickel, and may now be dried on the filter paper at 100° C.; but it is preferable to detach the partly dried substance from the paper and continue the drying in a capsule, otherwise it adheres so forcibly to the filter and contracts so much during the process that it becomes contaminated with the fibre. Thus prepared the substance is obtained as a heavy black mass, which is apparently unaltered by exposure to the air at ordinary temperatures. It is easily soluble in sulphuric or hydrochloric acid with evolution of hydrogen, and also in nitric acids, whereby ruddy fumes are given off. In each case the ordinary green nickel salts are formed.

Carbon monoxide is without any action upon it. It is soluble in potassic cyanide, hydrogen being liberated. If the solution takes place in a non-oxidising atmosphere and with excess of alkali, the red cyanide is partially reproduced. It is also powerfully magnetic, being strongly attracted by a magnet. Tested qualitatively it gave no trace of cyanogen. Up to the present I have not succeeded in preparing it in a state of purity, as during the reduction the glass vessels are attacked by the alkali, in consequence of which the preparation contains some silica, &c.; nevertheless it is of sufficient purity for its composition to be determined. This was done by acting on the substance with a neutral solution of argentic nitrate. Decomposition begins at once and metallic silver separates out, often in brilliant spangles. On completion of the reaction (twenty-four hours) the precipitate may be filtered off and washed first with water and then with hot dilute sulphuric acid; the metallic silver and dissolved nickel may then be estimated in the usual way. Separate portions were taken for the estimation of impurities and water of combination; the latter had to be carried out in a combustion tube, catching up the water in calcium chloride tubes, owing to the oxidation of the precipitate at elevated temperatures. Many analyses were made, but one will suffice, as they are all very similar.

Weight of substance taken, 0·5974 grm.

	Found.
Ni	0·4251 grm.
H_2O	0·0958 ,,
SiO_2	0·0350 ,,
Alkali, &c..	0·0021 ,,
Oxygen (diff.)	0·0394 ,,
Silver reduced	1·0450 ,,

A quantity of gelatinous silica dried under similar circumstances gave on ignition slightly over 10 per cent water, so that it is safe to assume that the silica contained in the substance contained approximately this amount of water. If, therefore, the impurities and this water be deducted, the following is the percentage composition:—

	Found.	Theory for M_3ONH_2O.
Ni	76·34	77·20
O	7·08	7·01
H_2O	16·57	15·78

Again, by considering the relation of the reduced silver to the nickel, the same result is arrived at.

Total nickel found	0·4251 grm.
Nickel equiv. of silver	0·2840 ,,
Difference	0·1411 ,,

Complying exactly with the equation—

$$M_3O+4AqNO_3=2Ni_2(NO_3)+NiO+4Aq.$$

There can therefore be no doubt that it is a hydrated suboxide of nickel with the formula $Ni_3O_2H_2O$. Such a compound was foreshadowed from the results of the preliminary experiments mentioned in the previous communication, although from the position of nickel in the periodic system Ni_2O might rather have been expected. This, however, cannot be reconciled with the results of the analysis of the oxide, prepared at different times and under different conditions. It is just possible also that this is the oxide which is formed when alkaline stannous chloride is allowed to act on hydroxide of nickel. On heating a mixture of the two substances, the green oxide takes a darker shade and finally becomes quite black; but inasmuch as the product is rendered highly impure with different tin compounds, I have not yet decided the matter.

Nouméa, New Caledonia,
November 30, 1894.

THE SOLUBILITY OF BASIC SLAG.

In a paper read before the Cleveland Institute of Engineers,* C. H. Ridsdale discusses certain statements published as Professor Wagner's, and current impressions relating to the "fertilising activity" of various makes of basic slag as measured by the citrate solubility of the phosphoric acid, some of which, particularly the third, were in his opinion misleading.

1. That this solubility represented or was closely parallel to the availability for plant life under actual agricultural conditions.
2. That the more soluble slags were also generally higher in silica.
3. That slags having a higher "percentage solubility" were more valuable than those with a low percentage solubility, though the former might contain only 10 per cent or 12 per cent total phosphoric acid, as against 17 per cent or 18 per cent in the latter.

An instance of the third proposition cited was in a pamphlet, which was a translation of a paper by Professor Wagner published presumably for farmers, in which were tables giving numerical values to slags of different makes, which as printed were altogether incorrect, a slag having 8·44 per cent soluble phosphoric acid being valued at 100, whilst one having 14·48 per cent, nearly twice as much, was only valued at 81, simply because only this percentage of the total phosphoric acid was soluble. These values held good per unit, but this had not been stated, and in consequence of such statements entirely false impressions had been created, which it was important to remove, as they might be most serious to makers and farmers.

He had carefully examined the six crystalline constituents of basic slag, three of them phosphoric, and three non-phosphoric, some of which Mr. Stead and himself had discovered and described for the first time to the Chemical Society and Iron and Steel Institute early in 1887.

He had also examined a number of basic slags, including three of the North Eastern Steel Company's make (which gave very good results), and a number of other British makes, all of a degree of fineness as put on the market, as well as siliceous cinders for comparison. Of these he had determined the "citrate solubility" by Professor Wagner's method, together with the effect of friction on the same, the composition and the carbonic acid water solubility, and had drawn up a number of tables and diagrams (which were shown by means of lantern slides kindly prepared by Mr. Stead) illustrating the results.

He showed that that portion of the phosphoric acid not soluble in the first treatment by the "citrate" test as conducted, is not necessarily unavailable for plant life, even during the first year, as extended conditions such as:

1. More solvent.
2. Greater degree of fineness.
3. Longer time.
4. Friction such as may take place between the earth and the slag, &c., may render it all soluble.

That pure tetrabasic phosphate of lime, whether natural (as in the transparent plates) or artificial (as prepared synthetical by Mr. Stead), are completely soluble, and as readily so as the blue crystalline variety, if the citrate used is proportioned to the phosphoric acid present.

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* January 14, 1895, with which is incorporated an appendix prepared afterwards.

That increased quantities of poorer slags, containing the same quantity of soluble phosphoric acid as richer varieties, and which should when treated with fixed quantities of solvent (as would under actual agricultural conditions be the case) yield an equal amount, do not, but yield much less.

He dissented strongly from the expression of results in terms of "percentage solubility," and drew many comparisons between this and the absolute solubility.

His earlier experiments showed the alleged close relation between the silica content and the "percentage solubility" to have almost as many exceptions to as examples of the rule, and that there was a point beyond which the higher the silica the less the solubility. He contended that only practical tests extending over years could show the real value of slags of different degrees of solubility, and that next to this would come carbonic acid water tests.

He therefore sought further for the principles governing this, and after determining what bodies the citrate solution dissolved preferentially, as well as from a close study of the behaviour of whole series of samples, and of other evidence adduced, felt there was good ground for the following conclusions.

The "*Percentage Solubility*" depends on:—

1. The actual content of phosphoric acid varying inversely to it.
2. The neutrality or freedom from excess lime (and possibly certain other bases).
3. That silica does not *per se* increase this, but only:—
    - *a*. When it combines with and thus neutralises excess of lime, and possibly certain other bases.
    - *b*. When as a condition of the presence of a large quantity of silicate of lime (which silicate appears not to interfere with the solubility in the quantities in which it is generally present) there is only a low total percentage of phosphoric acid present.
4. That silica decreases this when present in quantities greater than required in 3, or sufficiently large to bring about the formation of silicates of iron or manganese.
5. That excess of oxides of iron and manganese have a very small effect, almost negligible when compared with that of lime, the actual solubility being the resultant of the inert action of each of these conditions as are present.

The *Absolute Solubility*, or actual amount dissolved, depends on:—

1. The actual content of phosphoric acid, varying directly with it, and in other respects following 2, 3, 4, and 5.

From these conclusions he showed that if any maker's slag has a poor solubility it is necessary in the first place to determine to which of these causes this is due, in order to decide what cure to adopt, or whether any is practicable.

THE SECRET OF THE BROWNIAN MOVEMENTS.*

By R. MEADE BACHE.

(Continued from p. 48).

The account of the views of Herr Wiener in the *Jahresberichte* makes an important omission. It devotes itself chiefly to reciting what, in his view, does not cause the brownian movements, but does not mention precisely to what he does ascribe them. Herr Wiener says, in the last paragraph of his article, in *Poggendorf's Annalen*, 1863: "The weight of the preceding conclusion, that one cannot ascribe the trembling movement to any exterior cause, is very greatly added to by the ascertained fact that the diameter of the similarly moved water masses is so small that it nearly corresponds with the wave-length of red light, and still more closely with that of radiant heat." This passage gives the key-note to his views on the brownian movements. After a most elaborate series of experiments, in which he measured on a micrometrically divided glass slide, with the addition of diagonal lines, and by watch, the range and the time of the movements, he reached his most important conclusion, that, because the dimensions of the aforesaid wave-lengths of light and heat have a certain close correspondence with the diameters of the minutest particles and water masses, they form the moving impulse of the motions of the particles. He pictured to himself that the ether surrounding the particles, being continuous with the ether of space, acts, through the rays of light and heat on the particles and minute water masses, generating in their interaction, as the visible resultant of the forces in play, the movement of the particles in suspension in aqueous solutions. But if the cause of the movements assigned by Herr Wiener were the true one, the same cause ought to be operative in the case of alcohol and in that of the fixed and volatile oils; but it is not. This conclusion of Herr Wiener's seems to me to be derived from the unsatisfactory fact of a coincidence, of which kind of proof we habitually perceive more than enough to obscure, bewilder, and often to baffle our feeble efforts to penetrate beyond the veil of phenomena, of things as they seem, to the everlasting noumena, things as they are, near the inscrutable throne of nature.

I will not weary my hearers with the recital of the numerous details of my own experiments, the names of the substances that I tried, the modes in which they were treated, the manipulations of various sorts necessary to the prosecution of the work. Everyone knows the difficulties that will arise in new investigations, which will themselves suggest the means of countervailing them as the work proceeds. In this particular case one difficulty was to obtain finely enough divided matter in other liquids besides water. It may be interesting to mention that I did not read anything on the subject until my own experiments were nearly finished. By this course I avoided any possible bias expressed or implied in the directions to be pursued and the conclusions to be drawn, and I had ultimately the satisfaction to perceive, as I had often before observed, how, owing to the constitution of the mind, men necessarily follow the same general and often particular track in their procedures. It is not in the course they follow that they differ much, but in the conclusions which they reach in pursuing what is virtually the same way. Fortunately for me, constrained to be absent for months in the field on geodetic duty, and at all times constantly engaged at my profession, night still lent itself to my slowly accumulated results. That the investigation was most interesting, I need hardly say.

As electric currents have been demonstrated in the human body, I naturally thought that all slight differences of tension between the liquid and particles, or in the liquid itself, might set up electric currents. Therefore I passed the galvanic current through liquids filled with particles, watching them carefully. There was not the slightest visible effect thereby produced on the movements of the particles. If the movements had been produced by electric currents, then so strong a current as I often passed through a drop of water ought to have left no manifestation of movement possible from the necessarily weak, if actually existing, currents supposed to be actuating the particles. The molecular movement, so-called, is, as described by Herr Wiener, a zigzag one, but that term does not exactly convey the peculiarity of the motion. It is a combination of a jerky, wobbling movement, performed within determinate bounds, entirely irrespective of the sweep of currents in the liquid, or even

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* Read before the American Philosophical Society, April 20, 1894. —From the *Proceedings of the American Philosophical Society*, xxxiii, No. 145.

of the effects in some cases of terrestrial gravity, and in no case seemingly affected by the influence of local gravitation of particle to particle. Taking the vermilion of the sulphide of mercury, as finely divided as it can be made, and turning the microscope at even a slight angle from the vertical, the effect of terrestrial gravity on the particles becomes at once apparent, but taking the carmine, reputedly made of cochineal, the particles are not affected in the slightest degree by terrestrial gravity. Of course it is hardly neeessary to say that any solution should be weak, in order to allow the substances under examination to receive the finest division of which each is susceptible as dissolved. The specific gravity of sulphide of mercury is not only much greater than that of cochineal, but additionally it is not susceptible of nearly so minute division as cochineal is. Of all substances that I experimented with, cochineal seemed to be that which is capable of the finest division, and at the same time of the most brilliant illumination. Gamboge, which appears to be the substance of predilection among many persons to experiment with for the brownian movements, offers nothing comparable to the brilliancy and the fineness of particles of carmine derived from cochineal. With a weak aqueous solution of carmine one may see by daylight, on a background of faint blue, and by ordinary artificial light, on a golden one, thousands of tiny particles, bright as sparks of ruby, shimmering and performing their independent evolutions over the field of view.

Just as one sees a boat managed by an unskilful helmsman pursue its erratic way in going about, being taken aback, or heeled over by a flaw of wind, without for a moment attributing its movement to currents or any other cause but the true one, so the constant observer of the brownian movements knows full well that the particles themselves are moving, not being moved by currents or by gravitation towards the earth or among themselves. He, from the first, recognises the fact that the smaller the particles are, the more vivid is their movement. He recognises another, that, although many large particles do not, as masses, move at all, yet the larger masses are all alive, as it were, with smaller ones, seen clearly around their periphery, on the silhouette of which they are seen plying like banks of oars in an ancient trireme. He is struck with and convinced of still another thing, that whereas one might expect to find that all particles would manifest an attraction for each other through gravitation, and that the larger and largest, but all in proportion to their relative size, would attract and absorb the relatively smaller and smallest ones, nothing of the kind occurs, but the smaller, down to the smallest, go their own way, sometimes even touching the largest and bounding off and away as if they do not, as indeed they do not visibly, submit to the force of gravitation. Of course they cannot escape the influence of gravitation, whether terrestrial or among themselves, but the effect of gravitation upon them is masked, in what manner will appear later.

It seemed to me that magnetic earth-waves might affect particles in such delicate suspension as those of which we are speaking, some of which are no greater in diameter than 1-100,000 of an inch, seen under various powers capable of magnifying from 650 to 1300 diameters. Accordingly, I have placed the particular fluid under examination in the lines of force of a permanent magnet, with the magnet on one side and the keeper on the other of the drop of fluid. Concentrating the gaze on individual particles, to observe if their movement were modified, and then on others in succession, and often repeating the experiment, nothing could be observed other than the movements existing before the magnet had been brought into requisition. The only kind of particles susceptible to the influence of the magnet were those of precipitated iron, but iron is always obedient to the magnet.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 8th, 1895.

Prof. A. W. Rücker, F.R.S., President, in the Chair.

The Treasurer, Dr. Atkinson, presented his report for the year 1894. The balance-sheet showed a somewhat larger expenditure than in previous years; the increase being partly due to the new system of publishing abstracts, partly to the rent of rooms and the expenses of tea. The balance in the bank had increased by about £33 during the year, but the Treasurer said that, strictly speaking, the Society had trenched on its capital to the extent of about £30, and that this would probably be the last report for some time to come which would show a balance in favour of the Society. The assets of the Society exceeded its liabilities by £2642 0s. 5d.

Prof. Carey Foster asked whether it would not be possible, in estimating the assets of the Society, to make some allowance for the stock in hand.

Dr. Atkinson replied that that had not hitherto been done, and the difficulty would be to assign a money value to the stock. The stock of the works of Joule and of other memoirs was, of course, decreasing, while the sale of the *Proceedings* was becoming somewhat greater. As regarded the securities of the Society, their actual value would be about £200 or £300 more than appeared on the balance-sheet.

Prof. Rücker said that the Society had deliberately entered upon a policy of expansion, and that they must be prepared to find the expenditure increasing. On the other hand, it was hoped that, by making the Society more attractive, a greater number of persons would be induced to join. In view of the great advantages now enjoyed by members, there had been some suggestion of raising the subscription, but in any case he thought that they might look forward to the future with confidence. The report was then moved and adopted.

The next business was the election of Officers and Council for the year 1895-6, and Messrs. Rhodes and Yule, being asked to act as scrutators, collected the balloting lists.

Prof. Carey Foster proposed a vote of thanks to the Lords of the Committee of the Council on Education for having allowed the Society to meet at the Royal College of Science. At the commencement of the life of the Society, its founder and first president, Guthrie, had obtained permission for the meetings to take place at South Kensington, and the Society had continued to meet there until their recent migration to the rooms of the Chemical Society. The vote of thanks was duly seconded and was carried unanimously.

Major-General Festing then proposed, and Mr. Croft seconded, a vote of thanks to the auditors, Messrs. Inwards and Trotter. This also was carried.

Mr. Trotter then proposed a vote of thanks to the retiring Council. They had shown an energy which was rare in such societies, and had inaugurated an active and original policy which must prove of the greatest benefit to the Physical Society and to physical science generally. Carried unanimously.

Mr. Elder gave notice of a proposed alteration of the Rules, the object being to allow the Council, under certain conditions, to admit persons into the Society without requiring from them the usual number of recommendations from members. It was pointed out that sometimes eligible persons, especially those resident abroad, were unable to enter the Society because they were unknown to any of the existing members. The motion to sanction the proposed alteration was put from the chair and carried, but this decision will need to be confirmed at a subsequent meeting, of which due notice will be given.

Mr. Rhodes then read the following list of Officers and Council elected for the year 1895-6 :—

President—Captain Abney.

Vice-Presidents who have filled the office of President—Dr. Gladstone, Profs. Carey Foster and Adams, Lord Kelvin, Profs. Clifton, Reinold, Ayrton, Fitzgerald, Rücker.

Vice-Presidents—Mr. W. Baily, Maj.-Gen. Festing, Prof. Perry, Dr. Stoney.

Secretaries—Messrs. Blakesley and Elder.

Treasurer—Dr. Atkinson.

Demonstrator—Prof. Boys.

Other Members of Council—Mr. Shelford Bidwell, Prof. Crookes, Messrs. Fletcher, Glazebrook, G. Griffith, Profs. Henrici, Minchin, Mr. Swinburne, Profs. S. P. Thompson and S. Young.

Prof. Rücker then vacated the chair in favour of Captain Abney, and the meeting being then resolved into an ordinary meeting,

Mr. W. B. Croft gave "*An Exhitition of Simple Apparatus.*"

An optical bench was shown which consisted of a wooden lath of rectangular section, furnished with a millimetre scale, and clamped on to the table, together with three flat wooden blocks, whose contacts with the table and the lath left them only freedom to slide in a direction parallel to the scale.

Another apparatus was designed for observing anomalous dispersion. A cork supported two rectangular pieces of microscope cover-glass, which were inclined at a small angle to one another; and a drop or two of a strong alcoholic solution of fuchsine being introduced between them was maintained in position by capillary action. Photographs were shown of Chladni's sand-figures, some of the forms being of an unusual character.

Mr. Croft also exhibited a polariscope in which the polariser was a thin piece of glass stuck into cork by means of black sealing-wax, and the analyser a plate of tourmaline; as well as a miniature model of Grove's gas battery.

Photographs of some curious optical phenomena were projected on the screen, including 12-rayed stars, seen on looking at a bright source of light through certain specimens of mica, and pairs of intersecting or non-intersecting circles of light obtained under similar circumstances with (doubly-refracting) fibrous calcite. These last, it was suggested, were similar in origin to the curves obtained by reflection at, or transition through, a diffraction-grating held obliquely.

Clock-springs broken by frost were also exhibited, each spring having given way in a very great number of places simultaneously.

Dr. Johnstone Stoney said that many years ago he had published in the *Transactions of the Royal Irish Academy* an investigation of the circles seen in fibrous calcite, and had shown geometrically that they had nothing to do with the regularity of the fibrous structure, but were due to reflection and refraction within the crystalline plate. The distribution of the planes of polarisation round the circumferences of the circles was also accounted for by his investigations.

Mr. Price said he had found that when a clock-spring during the process of hardening was kept in shape by wires, subsequent fracture was most apt to occur at those places where the wires had been in contact with the spring.

Mr. Rhodes asked if Mr. Croft had ever tried Newton's experiment of admitting sunlight between two sharp edges inclined at a small angle to one another. He had not been able to obtain the hyperbolic bands described by Newton.

Mr. Croft said he had not tried the experiment exactly in that form.

Capt. Abney said that the experiment had succeeded very well in his hands.

Mr. S. Skinner read a paper "*On the Tin Chromic Chloride Cell.*"

He said that his attention had been attracted to the cell by an account published by Mr. Case, of New York. The cell had been stated to give no E.M.F. at ordinary room temperatures, while it gave a considerable E.M.F. at 100° C.

The author had found that when the cell was directly connected up to a galvanometer, there was no current at ordinary temperatures, and some current at 100° C., but when he had measured the E.M.F. by Poggendorff's method he had found 0·44 volt at 15° C., and 0·40 volt at 97° C. The cell, as originally described, consists of a tin plate and a platinum plate immersed side by side in a solution of chromic chloride; when the temperature of the cell is near to 100° C. and the poles are connected, the following reaction occurs :—

$$Cr_2Cl_6 + Sn = 2CrCl_2 + SnCl_2;$$

and when the poles are disconnected and the cell cooled, the reverse change takes place. The author prefers to use as electropositive metal an amalgam of tin and mercury instead of a tin plate, so that when the tin precipitated during cooling falls to the bottom of the solution, it is re-dissolved in the mercury, and the cell has regained its original state. When silver nitrate solution is added to chromic chloride, only two-thirds of the chlorine comes down as silver chloride, and this has led the author to suppose that the proper formula for chromic chloride is $2CrCl.Cl_2$. Hence he works out the electrolytic action by means of a Grotthus chain.

Prof. Rücker asked whether a change of polarisation would explain the behaviour of the cell at different temperatures.

Prof. Carey Foster asked whether the reversed chemical action on cooling from a high temperature were accompanied by a reversed E.M.F.

Mr. Skinner said no; the tin was precipitated throughout the solution, and not at the surface of the tin plate, so that no E.M.F. of the kind was to be expected.

Mr. Appleyard thought that Prof. Minchin had used tin chloride cells with two tin plates for electrodes, the cells only working when one plate was illuminated.

Mr. Trotter wished to know whether heating the cell supplied energy to it, or simply removed an obstacle in the form of polarisation.

Mr. Skinner thought that heating acted by removing an obstacle.

Capt. Abney—And so doing work.

NOTICES OF BOOKS.

What is Heat? A Peep into Nature's most Hidden Secrets. By Frederick Hovenden, F.L.S., F.G.S., F.R.M.S. London: W. B. Whittingham and Co., Limited. 1894. 8vo., pp. 350.

This is a very remarkable book and the outcome of a remarkable work. The author is a busy man of the busy world, who spends his leisure in the investigation of natural phenomena, not by the more laborious methods of what we may call "official science," but on an original and independent plan, characterised by a boldness amounting almost to audacity, and quite refreshing as a subject of contemplation and a relief from the uncompromising severity of mathematico-physical treatises. We who spend our days in laboratories in the hum-drum work of worrying out particular issues and proximate truths can hardly refuse a full measure of admiration of a thinker who quietly brushes aside the monumental structures which we owe to the genius and patient elaboration of such philosophers as Joule, Clausius, and Maxwell, and pokes fun at a generation of physicists who have been proud to fall into line under their leadership. To put it briefly, the author deliberately poses as a rebel. We know from history that the only justification of rebellion is success; the dire alternative is usually the loss of a head.

This issue the author does not hesitate to challenge. It is true that he exhibits an occasional distrust of his ability to carry the position, and is inclined to plead with his friend the enemy. But the pleading is perhaps rather with "the layman," by whom, to use the author's words, "the verdict will in the main be given, and to whom the issues are of the greatest importance."

The author is anxious that the book shall make its mark, not merely on its self-contained merits, but because he feels a further call to attack the problems "what is electricity"? "what is life"? for the solution of which he is of opinion "that science has sufficiently advanced." This appeal perhaps is hardly ingenuous: it adds to the responsibility of the critic by introducing contingent and somewhat irrelevant issues. We confess that our judgment of the work would not be uninfluenced by this promise of contributions to even more burning subjects than the theory of heat, subject to favourable consideration of "these presents." Whether the author will feel encouraged by our appreciation of his work to address himself to this magnificent crescendo of effort we have no opinion. We deliberately close our eyes to the vista of scientific speculations opened up by the too suggestive preface, and shall be content to arrive at a fair judgment of the matter of the book as it stands.

The first section of the book is a criticism of "mathematical and physical concepts." The aim of the discussion is to disestablish the mathematician from what we should have considered his unquestionable position of leadership in the affairs of science. Mr. Hovenden twits him with the unreality of the most ordinary of mathematical operations. Thus "let us multiply -100 (*i.e.*, minus 100 objects or units) by -100 operations. The latter expression is unthinkable. But the mathematician says the result of the process, the product, is (plus) $+10,000$ objects!" This is then worked by the author to an apparent *reductio ad absurdum* as follows:—

We take two bowls, a and b. In a are 100 objects. We take the 100 objects out of a and put them in b. This is expressed mathematically $a-100$, $b+100$. Now multiply the contents of bowl a (-100) by -100 times, and then, says the mathematician, there are 10,000 objects in that bowl! "Can the operation be performed"? says the author. "Mr. Mathematician" is directed to take two bowls and 100 marbles and perform "the operation"; "then" (by inference) "we can believe in your fundamental ideas."

We don't know whether any mathematicians will read this book, and if so whether they will resent this and other efforts to materialise and ridicule their symbols and operations.

It appears to be a necessary part of the author's scheme to clear away the mathematical methods of handling quantities with which his own are irreconcilable. That is his own confession, implied in every section of the book. The author enters on the issue with a light heart and light language. He evidently has not studied De Morgan's "Budget of Paradoxes." There are many warnings in this classic of which he might have availed himself for the strengthening of his indictment. He will be the first to admit that it might have been stronger, and most mathematicians will agree. They will also be quite ready to stand aside in favour of Mr. Hovenden should he be able to climb the inaccessible peaks of "ethereal" truths by the direct method of "sensible" observation. And they will note that he claims to have done this.

Section II. is devoted to destructive criticism of the kinetic theory. We commend this section, as indeed the preceding, for a collection of well-chosen excerpts from the writings of Clerk Maxwell and others who have contributed to the elaboration of this remarkable theory. These excerpts constitute a fair general statement of the theory in question, to which the author advances certain particular objections. Instancing a silver coin of date B.C. 200, we are confronted by the author with the paradoxical hypothesis that the ultimate atoms of this extremely concrete object are, and have been, according to the "Kineticians," in a condition of intense heterogeneous motion. The second is based on the comparison of the condition of water with that of the gases of which it is composed, or into which it may be decomposed, respecting which we read in the book, "the temperature of the gas is exactly the same as was the water as measured by the thermometer, proving there is no more motion in the gas than there is in the water; so the dynamical theory cannot be true. The third "negation" of the theory is that supplied by the effect of releasing gases from pressure, and allowing them to impinge on the face of a thermopile, causing the reaction of "cold," together with the converse experiment of blowing upon the instrument with bellows, causing the opposite effect.

We do not propose to traverse the author's arguments. He is evidently, from the later section of the work, so entirely convinced by his "sensible" observations of being in possession of facts (and the key to them), which categorically upset every cardinal position of the modern physicist, that argument looks a little like trifling.

The succeeding section on "Gravitation and Weight" is similarly devoted to correcting "the confusions with which the specialists have surrounded themselves." Clerk Maxwell and Lord Rayleigh are especially singled out for treatment on account of their pronouncement that gravitation is not a force.

The section concludes with a statement of "the only concepts which can explain the facts." The position not being arguable, therefore—with the author—the critic's task resolves itself into that of committing these further innovations to those who find rest in lucid finalities rather than in the complex equilibrium of proximate gropings.

The last sections of the book are the most original by far. They contain a careful description of a number of very interesting experiments and observations, preceded by a "statement of the case" or, *à priori*, formulation of the author's view of the micro-cosmos. This view is nothing less than remarkable. There are very few scientific men who are prepared with anything like a complete *credo* in regard to the constitution of matter, or the still more "elusive" quantity known as "ether." Mr. Hovenden has given us an object-lesson of boldness in reducing the results—evidently of years of thought—to a comprehensive statement in twenty-three "articles." The author's most important conclusions are that "the ether" is an "anti-gravitating fluid"; that the atoms and molecules—the ultimate forms of matter—are of variable form and dimensions; the difference in dimensions is due to variations "of the quantity of ether held by them at a given moment, and is what is called the *temperature* of the atom or molecule"; and lastly that both *ether* and *molecules* may be brought to visual demonstration, may be *seen* under conditions which it has been a main endeavour of the author to devise.

As we said, these extraordinary views are formulated as a "statement of the case," preceding the experimental and demonstrative section of the book. In these experiments the author shows a good deal of ingenuity. Every student accustomed to the strictly quantitative methods of modern science would find himself very much puzzled by the paradoxical observations which Mr. Hovenden is able to create and put before him in such form as to be undeniable. His intuitive scepticism would at once suggest the question: Can these observations involving not a single quantitative measurement constitute a destructive criticism of a science which only began to move with the entrance of the quantitative method, and has progressed *pari passu* with the reduction of the phenomena to mathematical expression? His most natural criticism would be "there must be something wrong somewhere," and he would proceed to vary the conditions of the demonstrations in every possible way with the view of locating that something.

However, it is quite impossible in the compass of this brief notice to follow our supposed student of the modern order in a detailed criticism of the phenomena designed to upset his cherished "apple cart." As we said at the beginning, the author is a rebel, and justifies his rebellion so far that he commits himself to a plain and categorical description of phenomena which he finds irreconcilable with the current theories of thermodynamics.

Heterodoxy is always interesting—sometimes from the matter of the dissent, more often from the form. It plays an important part in history, though we are bound to say a diminishing part in the history of the natural sciences.

The book we have thus briefly noticed is an extraordinary manifestation of the spirit of heterodoxy in a domain where it often receives short shrift. Mr. Hovenden knows his responsibility in this matter. We commend his work as an extremely interesting study to the metaphysician, and as affording ample entertainment to physicists not too exclusively dominated by the formal and academical view of their science or sciences.

OBITUARY.

Dr. GERHARD KRÜSS.

We have just learned, with profound regret, that Dr. Gerhard Krüss, Extraordinary Professor of Chemistry in the University of Münich, died on February 3rd at the early age of thirty-five years. Dr. Krüss was universally known and admired as founder and editor of the *Zeitschrift für Anorganische Chemie.* He was a worker from whom the philosophy of chemistry had much to hope.

CORRESPONDENCE.

ARGON.

To the Editor of the Chemical News.

Sir,—When lecturing on the atmosphere to my elementary class, it was necessary to discuss the new gaseous constituent announced by Lord Rayleigh and Professor Ramsay at the last meeting of the British Association, and I ventured to propound the theory that the new substance is an allotrope of nitrogen. The density of the gas discovered was given as 19·09, but it was admitted that some ordinary nitrogen still remained. If this last quantity of N_2 be removed, I anticipate the density would be 21; and the molecule of the allotrope be N_3.—I am, &c.,

Jas. Braik Mason, F.C.S.

Laboratory, Y.M.C.A., Constitution Road,
Dundee, February 6, 1895.

BORON CARBON BATTERY.

To the Editor of the Chemical News.

Sir,—In reply to Mr. C. J. Reed's remarks (Chemical News, vol. lxxi., p. 63), permit me to ask the writer where he obtains the information from as regards the existence of a platinum element in the battery described by me, while at the same time the title of the battery is distinctly stated "the boron carbon battery." Again, he uses the peculiar expression, as regards voltage, in "something over two of his three volts." Is this a Yankee bull, or does Mr. Reed expect one cell to dry up Niagara?—I am, &c.,

H. N. Warren.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

THE PERIODIC LAW.

To the Editor of the Chemical News.

Sir,—In your last issue you print a short paper by Dr. Johnstone Stoney, in which he refers to the Periodic Law. In it, after referring to the probability that the free hydrogen has passed into space, he remarks: "The six other elements between hydrogen and lithium seem not to have been able to enter into, or remain in, combination under the conditions that prevailed at some stage of the earth's past history, and so these escaped—unless, possibly, a compound of some of them may yet be found." For convenience, he names these elements infra-beryllium, &c.

Now, I would ask, have we any right to say that Mendeleeff predicts any such elements, or that his table is intended to indicate that they exist? The table is printed at the beginning of vol. i. of "The Principles of Chemistry" (English Translation). Here four of the six blanks are filled in with hydrogen compounds. I would also point out that there is nothing in this table to show that Mendeleeff believes that other elements will be found to come between F and Na. Table III. in the second volume of the above-named work clearly shows this. Here we have the elements arranged in the order of their atomic weights. In note [6] we read:—"In this column the sign ∼∼∼∼∼∼∼∼∼∼ placed between some of the symbols indicates that these are unknown intermediate elements according to the periodic system, and the figure indicates the number of such unknown elements. Thus, between Di and Yb there are fourteen elements wanting. It is probable that certain of the rare elements which have been discovered, but are as yet insufficiently investigated, enter into these interspaces." The first sign of the kind appears in the table between Mo and Ru; the series up to this point being regarded as complete, for no missing elements are indicated either between H and Li, or between F and Na. As Douglas Carnegie, in his very excellent article on the Periodic Law ("Watts' Dict. of Chemistry") remarks:—"Mendeleeff expressly omits Series 2 in making some of his generalisations." The elements from Li to Mg are regarded as "typical elements." Their classification is admittedly unsatisfactory, and it would be unwise to draw sweeping conclusions from the table alone.—I am, &c,

R. M. Deeley.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 4, January 28, 1895.

Raoul Pictet addressed to the Academy a new memoir entitled "Study of the Constitution of liquids and their Vapours at Temperatures near the Critical Point by Solutions of Solids in these Vapours."

A. Duponchel addressed two new memoirs concerning the "Adaptation of the Principles of the New Cosmogonic Theory to the Interpretation of the Formulæ of Chemical Combinations."

Stan. Millet addressed a "Project of Communication with the Planet Mars."

These memoirs were all referred to Commissions.

The Perpetual Secretary announced to the Academy the loss it had sustained in Dr. Gaston de Saporta, who died at Aix, on January 26, 1895.

Preparation and Properties of Iron Boride.—Henri Moissan.—The author has proved that at the temperature of the arc carbon unites with the metals, producing crystalline carbides, perfectly definite, such as aluminium-carbide, and the alkaline-earthy acetylides. Boron and silicon form in like manner series of definite crystalline compounds. The study of these new series will enrich chemistry with bodies, often very stable, some of which will doubtless admit of industrial applications, and will probably supply useful indications for determining the valence and the classification of the elements. Iron boride may be obtained by the action of boron chloride upon reduced iron, or by causing boron to act directly upon iron. Iron boride occurs in brilliant crystals of several m.m. in size, of a grey colour slightly yellowish. Its sp. gr. at 8° is 7·15. The crystals are stable in dry air or oxygen, but in presence of moist air they are covered with an ochreous layer. If heated in a current of chlorine at redness they are attacked with incandescence, and the chlorine unites with the boron. Bromine attacks this compound more readily, forming a double boron and iron boride. Iodine has no action at 1100°. It is the same with hydriodic acid. Oxygen attacks amorphous iron chloride more easily than the crystalline form. Amorphous boron is attacked by sulphur at a temperature little above its melting point. Potassium chlorate and nitrate do not attack iron boride at their melting-points, but if the temperature is raised, a reaction sets in and continues with incandescence. Melted alkaline carbonates rapidly destroy iron boride. The true solvents of iron boride are nitric acid and aqua regia. The theoretical composition of iron boride is—iron, 83·58; boron, 16·42. The figures actually obtained on analysis being—iron, 84·15; boron, 15·18, leading to the formula BoFe. On raising the temperature of the electric furnace at the moment of forming iron boride no other combinations have been obtained. At these high temperatures chemistry seems simplified, and we never obtain more than one compound of a very simple formula.

Action of an Electric Current on a Series of Metallic Sulphides in Fusion.—Jules Garnier.—The author concludes from his experiments that:—Sulphur combined with metals in a molten state in the absence of air, and traversed by an electric current, the electrodes (or at least the anode) being of carbon, there is doubtless a formation of carbon sulphide. In a mixture of molten metallic sulphides, excluded from air, and traversed by an electric current, the electric conductivity of the mixture remains *homogeneous* at each instant considered, increasing by degrees, in consequence of the successive elimination of the sulphur. As for the metals and the residual sulphur, they group themselves so that each elementary section of the bath, taken perpendicularly to the direction of the current, has the same electric conductivity. Setting out from such experiments it may be possible to explain certain phenomena observed, *e.g.*, the manner of the distribution of metals, sulphurised or not, found in veins.

Some Properties of Bismuth Sulphide.—A. Ditte.—Space permitting, this paper will be inserted in full.

Influence of the Ambient Medium on the Transformation of Amorphous Zinc Sulphide.—A. Villiers.—The author studies the influence of dilution, of the alkalinity of the liquid, of the presence of foreign salts, and of washing.

Carbonyl Bromide and Chloro-Bromide.—A. Besson.—Not adapted for useful abstraction.

Mixed Ether, or the Ammonium Derivatives of Hexamethyltriamido-triphenylmethane.—A. Rosenstiehl.—The author expresses by the collective symbol A the group $[(CH_3)_2N.C_6H_4]$, which does not admit of any modification in the metamorphoses. Hence, $A_3\equiv C—H$ represents hexamethyl-triamido-triphenylmethane, $A_3\equiv C—OH$ the carbinol, and $A_3\equiv C—Cl$ the corresponding chlorhydrine. This last substance is known in trade as crystalline violet. The alcohol, which acts as a solvent if we cause caustic soda to act upon $A_3\equiv C—Cl$, enters by its substance into the mol. to form bodies of the general form $A_3\equiv C—OR$, which are derivatives of the methane-oxymethane $CH_3—O—CH_3$. Their existence and their manner of formation brings into fresh prominence the alcoholic function which is one of the peculiarities of the rosanilines.

Acetic Ethers of the Sugars.—C. Tanret.—By the reaction of acetic anhydride upon glucose in presence of sodium acetate or zinc chloride the author obtains three crystalline pentacetic ethers, which he names α, β, and γ pentacetines.

Hexamethylamine.—M. Delépine.—The author has studied the molecular weight of hexamethylamine, its behaviour with mineral acids, the nature of its basic function, the formation of its substitution derivatives, the nitroses and their destruction by acids, and its hydrogenation.

The Coula Seeds from Congo.—H. Lecompte and A. Hébert.—The oily matter of these seeds, known as koumounou oil, is a trideine almost pure. It is a curious instance of a fatty matter containing only a single fatty acid.

Novel Practical Procedure for the Determination of Calcareous Matter in Arable Soils.—Antoine de Saporta.—This paper will be inserted in full.

Journal fur Praktische Chemie.

New Series, Vol. l., Nos. 11 and 12.

Complex Metallic Bases. Treatise I. Metallic Compounds of Thiocarbamide.—N. Kurnakow.—This elaborate paper does not admit of useful abstraction.

Communications from the Chemical Institute of the University of Kiel.—These communications comprise a first treatise by Th. Curtius on the derivatives of diamide with a closed atomic arrangement, and a second treatise by F. Wirzing on pyrazolin and some of its derivatives. Both these papers have already been inserted.

The Oil of the Root of Mignonette.—J. Bertram and H. Walbaum.—This paper is a communication from the laboratory of Schimmel and Co., of Leipzig. The root of the plant (*Reseda odorata*) contains a substance smelling of horse-radish. The oil is of a light brown colour; it has at 15° the specific gravity 1·067; it was slightly dextro-rotatory + 1° 30′ in a column of the length of 100 m.m. At the ordinary atmospheric pressure the oil began to boil at 255°, but with decomposition. Even under reduced pressure it does not distil without decomposition. If boiled with sodium hydrosulphocyanic acid was found in the residue, proving the presence of sulphur in nitrogen. Hence the oil belongs to the class of the mustard oils. From its almost quantitative conversion into phenylethylamine, it must chiefly consist of phenylethyl mustard-oil.

Two New Laboratory Appliances.—H. Lœssmer.—The pieces of apparatus here described and figured are an agitator and a water-bath.

Reduction of Aromatic Nitro-Compounds.—H. Lœssmer.—Orthonitro substances have the property of not being attacked by alkaline arsenites. If ordinary commercial orthonitrotoluol is heated with aqueous solutions of this salt it is coloured dark yellow. The oil, which after reduction contains chiefly paratoluidin, with small quantities of azoxy-compounds as an impurity, is several times shaken up with hydrochloric acid and finally distilled over with watery vapours.

The So-called Stereo-chemistry of Nitrogen and J. H. van 't Hoff.—Ad. Claus.—A controversial paper.

MEETINGS FOR THE WEEK.

Monday, 18th.—Society of Arts, 4. (Cantor Lectures). "Means for Verifying Ancient Embroideries and Laces," by Alan S. Cole.
— Medical, 8.30.
Tuesday, 19th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8. "Paraguay," by A. F. Baillie.
Wednesday, 20th.—Society of Arts, 8. "Rule of the Road at Sea," by Admiral P. H. Colomb.
— Meteorological, 8.
— Geological, 8.
— Microscopical, 8.
Thursday, 21st.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Meteorites," by L. Fletcher, M.A., F.R.S.
— Chemical, 8. Ballot for the Election of Fellows, "The Electromotive Force of an Iodine Cell," by A. P. Laurie. "Contributions to the Chemistry of Cellulose," by Messrs. Cross, Bevan, and Beadle. "The Melting-points of Mixtures," by H. Crompton and Miss M. A. Whiteley. "The Volumetric Determination of Manganese," by Messrs. J. Reddrop and H. Ramage.
Friday, 22nd.—Royal Institution, 9. "Atmospheric Electricity," by Prof. A. Schuster, F.R.S.
— Physical, 5.
Saturday, 23rd.—Royal Institution, 3. "Moore's Irish Melodies" (with musical illustrations), by Sir Alexander Campbell Mackenzie, Mus. Doc.

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THE CHEMICAL NEWS.

Vol. LXXI., No. 1839.

ON THE RATIO OF THE SPECIFIC HEATS OF SOME COMPOUND GASES.*

By J. W. CAPSTICK, D.Sc., M.A.,
Fellow of Trinity College, Cambridge.

The experiments described are a continuation of those of which an account was given in the *Philosophical Transactions*, vol. clxxxv., p. 1.

The apparatus and method of procedure were the same as were described in the former paper. Kundt's dust-figure method was used for finding the velocity of sound in the gas, and the ratio of the specific heats was calculated by means of the formula—

$$\gamma = 1{\cdot}408 \times \rho \times \left(\frac{l}{l'}\right)\left\{1 + \frac{1}{p}\,\frac{d}{dv}(pv)\right\},$$

the last factor being added to the ordinary formula in order to correct for the deviation of the gas from Boyle's law.

The densities and isothermal curves were determined experimentally.

The results are as follows:—

Name.	Formula.	γ.
Methylene chloride	CH_2Cl_2	1·219
Chloroform	$CHCl_3$	1·154
Carbon tetrachloride	CCl_4	1·130
Ethylene chloride	$C_2H_4Cl_2$	1·137
Ethylidene chloride	$C_2H_4Cl_2$	1·134
Ethylene	C_2H_4	1·264
Vinyl bromide	C_2H_3Br	1·198
Allyl chloride	C_3H_5Cl	1·137
Allyl bromide	C_3H_5Br	1·145
Ethyl formate	$HCOOC_2H_5$	1·124
Methyl acetate	CH_3COOCH_3	1·137
Sulphuretted hydrogen	SH_2	1·340
Carbon dioxide	CO_2	1·308
Carbon disulphide	CS_2	1·239
Silicon tetrachloride	CCl_4	1·129

From these and the results given in the former paper it is shown that corresponding halogen derivatives of the same hydrocarbon have the same γ, the statement being no longer restricted to the monohalogen derivatives of the paraffins.

The equality of the γ's of the two dichlorethanes, and of methyl acetate and ethyl formate, shows that the previously investigated case of the two propyl chlorides does not stand alone, but that it is probably true that isomeric bodies in general have the same γ.

From the results of the substitution-products of methane and ethane with more than one halogen in the molecule it is shown that, whether the first chlorine introduced into the molecule alters the value of γ or not, each chlorine after the first causes a fall in γ.

$SiCl_4$ has the same γ as CCl_4. SH_2 has nearly the same γ as some observers have found for OH_2, but CO_2 and CS_2 differ widely, whence it follows that, just as in the case of hydrogen and chlorine, the possibility of interchange of oxygen and sulphur without altering γ does not extend to the substitution of two atoms of sulphur for two of oxygen.

In the paper a proof is given of the formula—

$$\beta + 1 = \frac{\frac{2}{3} + \frac{1}{p}\,\frac{d}{dv}(pv)}{\gamma - 1}$$

for calculating β, the ratio of the rates of increase of intramolecular energy and translational energy of the molecule on a rise of temperature, and the constant β is given for the gases investigated.

It is shown that—

$$\frac{\beta + 1}{n}$$

is constant for the paraffins and their monohalogen derivatives, whence it follows that for these the ratio of the increase of mean total energy to the increase of kinetic energy of translation of the molecule is proportional to the number of atoms in the molecule.

ON THE

NATURE OF THE SUPPOSED NEW ELEMENT PRESENT IN THE ATMOSPHERE.

By T. L. PHIPSON, Ph.D., F.C.S., &c.,
Formerly of the University of Brussels, and the Laboratoire de Chimie Pratique, Paris.

In the series of papers published by me in the Chemical News during the last two years I have brought forward many facts and arguments to show that the primitive atmosphere of the earth consisted of nitrogen alone, and that the whole of the oxygen now present in the air is due to plant life.

In these researches it was found that all plants are by nature essentially anaërobic.

It was also pointed out that nitrogen is the only element that could have formed our primitive atmosphere, on account of its extremely neutral or inert character.

After having paid so much attention to the nature of atmospheric air, I was much interested in perusing in a recent number of the Chemical News (vol. lxxi., p. 51) the account of the laborious and ingenious experiments of Lord Rayleigh and Prof. Ramsay on the existence of a supposed new element in the air, to the extent of about 1 per cent, which had hitherto been overlooked.

The reading of their paper has convinced me that the substance is an allotropic form of nitrogen, and that the day will come when they will succeed in converting it into cyanogen, ammonia, and nitric acid. As they show, it was already in the hands of Cavendish in the last century, as a residue of the sparking of nitrogen and oxygen.

When bodies are changed to an allotropic condition in this way their characteristic properties are enhanced. So for oxygen its activity is greatly increased, but for nitrogen the inert character would become more apparent.

According to Lord Rayleigh's figures, the substance called "argon" would be 3 molecules of nitrogen condensed into two molecules, somewhat analogous to what Andrews found for ozone as compared to ordinary oxygen.

The Casa Mia Laboratory, Putney,
London, S.W., Feb. 9, 1895.

LORANDITE, A NEW THALLIUM MINERAL.

A new thallium mineral has just been described, under the name of Lorandite, by Professor Krenner, of Buda-Pest. The new mineral occurs sparingly, in association with realgar, at Allchar, in Macedonia. It is found as transparent crystals belonging to the Monosymmetric system, and having the form of plates or short prisms. Its colour varies from cochineal-red to kermesite-red. The mineral proves on chemical analysis to correspond to the formula $TlAsS_2$.

	Observed.	Calculated.
S	19·02	18·67
As	—	21·87
Tl	59·51	59·46

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* Abstract of a Paper read before the Royal Society.

AN ATMOSPHERIC PURIFIER.

By JOHN B. COPPOCK, F.C.S.,
Science Master, Camberwell Institute.

When a flocculent solid body falls through a fluid it drags down in its falling suspended matters contained in the fluid.

We should therefore expect that snow falling through the atmosphere will cleanse it by taking out most of the suspended matters. The present year has afforded many opportunities of getting a quantitative value for the purifying action of snow.

The first analysis gives figures yielded by snow collected in the suburbs of London, where the district is fairly open. This snow fell on January 13th, having a depth of 4 inches approximately. One characteristic of this snow was its great porosity, the crystals were also regular; both indicating that the snow was formed in a calm atmosphere.

The snow was melted and then analysed as water, the impurities being stated in grains per gallon.

Total solid matter	10·65
Mineral matter	5·75
Carbonaceous matter.. ..	4·90
Free ammonia	3·20
Albumenoid ammonia . ..	4·62
Oxygen to oxidise	0·721

A further analysis was made of snow from the same district after the fall of January 30th. The result was almost identical with the above figures; but this fact came out, that the first few strata of snow contained the largest amount of impurities. Fifty per cent of the snow's thickness yielded 75 per cent of the impurities.

An analysis of the snow of January 30th was also made upon snow collected in the quadrangle of Somerset House. The following shows the difference in the impurities. The physical condition of this fall was favourable to its picking up in its meshes much suspended matter.

Total solid matter	17·32
Mineral matter	6·25
Carbonaceous matter.. ..	11·07
Free ammonia	4·65
Albumenoid ammonia . ..	6·50
Oxygen to oxidise	1·16

The carbonaceous matter in each sample was ordinary soot particles.

These figures point out the value of a fall of snow from a manurial point of view, and also its value from a hygienic point of view. In a city where the air is often saturated with carbon particles, a fall of snow may be regarded as a mechanical contrivance of no mean value.

A NEW METHOD FOR THE ANALYSIS OF ZINC AND COPPER ALLOYS.

By H. N. WARREN, Research Analyst.

The following method of separation of zinc from copper and other allied metals, which was introduced by the author at the commencement of the present year, and is now being satisfactorily worked in several commercial laboratories, depends chiefly upon the superior affinity of magnesium to replace not only copper and metals of the same group, but by suitable means to effect a complete separation of such oxidisable metals as zinc, iron, &c. The method, although speedy and accurate, is perhaps better suited in cases where an approximate idea is known as to the nature of the alloy qualitatively. In the case of the sample presented being a brass alloy, which should, for convenience sake, be obtained in the form of filings, a suitable weighed quantity is introduced into a small conical flask, to which is added strong H_2SO_4 in proportion to the quantity of sample taken. On applying a gentle heat from a sand-bath for a few minutes, the alloy is quickly rendered soluble, and the whole diluted with water to a convenient bulk.

A few coils of magnesium tape are now introduced into the solution, and the solution maintained at about 100° F., until the whole of the copper is precipitated, which is ascertained by the absence of a red precipitate upon the addition of a drop of potassium sulphocyanide to the filtrate. The precipitated copper, which should be of a perfect red colour, is filtered, and finally washed into a tared platinum dish by the aid of a small quantity of ether, and dried in the air-bath, from whence the weight is readily obtained by the usual method. If tin, antimony, or other metals of the same group are suspected, the copper must necessarily be further examined. To the filtrate is added a somewhat strong solution of sodium acetate, and the whole raised to the boiling-point. By this means any free sulphuric acid is neutralised, all the iron that may be present is precipitated as tribasic acetate, and the sulphate of zinc present converted into acetate.

Into this is introduced a further quantity of magnesium, and in this instance the form of thick sheet or rod is better adapted than that of tape, the precipitated zinc being the more readily detached from the same. Upon the introduction of the magnesium, a brisk reaction follows, accompanied by a copious supply of hydrogen, the zinc being entirely precipitated, insomuch that not the slightest precipitate is obtained on the addition of ammonia and ammonium sulphide to the filtrate, the zinc thus obtained being treated as in the former instance, which, if successfully performed, shows very slight signs of oxidising.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending January 31st, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, February 11th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 161 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from January 1st to January 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

In all respects the chemical composition of the five Thames-derived waters in January is a little better than that of the corresponding samples for December. The effects of the floods have passed away, and although the severe frosts have checked aquatic vegetation and thus tended to diminish the oxidation of organic matter through the influence of plant life, this diminution is not perceptible, the organic matter being a trifle less than it was last month.

In spite of the difficulties of filtration when the surface of the filter beds are liable to be frozen, only three samples were recorded as "clear but dull," the whole of the other samples being clear, bright, and well filtered.

The rainfall over the Thames valley has been slightly in excess of the twenty-five years average, which is 2·26 inches. The actual rainfall has been 2·60 inches, showing an excess of 0·34 inch.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

ON THE ESTIMATION OF ALKALINE HYDRATES AND CARBONATES IN THE PRESENCE OF ALKALINE CYANIDES.

By J. E. CLENNELL, B.Sc.,
Chief Chemist, Rand Central Ore Reduction Company,
Johannesburg, S. Africa.

It is frequently a matter of technical importance to estimate rapidly, and with sufficient accuracy for practical purposes, the percentage of alkaline hydrate and carbonate present in the solutions of potassium or sodium cyanide used for the extraction of gold and other purposes.

The ordinary alkalimetric methods cannot be directly applied, owing to the circumstance that the cyanides of the alkali metals behave towards the ordinary indicators, such as litmus, methyl-orange, and phenolphthalein, as though the alkali metal were present as hydrate. A solution of a pure cyanide is alkaline to all these indicators, and remains alkaline, when titrated with hydrochloric acid, until the whole of the alkali metal has been converted into chloride, as in the following equation:—

$$KCy + HCl = HCy + KCl.$$

Thus 10 c.c. of a 0·53 per cent solution of pure potassium cyanide were titrated with normal hydrochloric acid, using phenolphthalein as indicator. It was found that 0·8 c.c. were required to destroy the pink colour of the solution. As 1 c.c. of normal hydrochloric acid corresponds with 0·065 grm. KCy, this indicates a percentage of 0·52 KCy in the solution.

Ten c.c. of a 0·45 per cent solution of commercial potassium cyanide were titrated with half-normal hydrochloric acid, using phenolphthalein as indicator. It was found that 1·35 c.c. of acid were required. Calculating as before, this indicates the presence of 0·044 grm. potassium cyanide, or 0·44 per cent in the solution.

In two experiments 20 c.c. of a 0·455 per cent solution of commercial potassium cyanide were titrated with decinormal hydrochloric acid. The end-point of the phenolphthalein reaction was much more indefinite and difficult to observe than when normal and half-normal solutions had been used, and was obtained in the two experiments at 13·9 and 14·1 c.c. of N/10 hydrochloric acid respectively. Taking the mean of these, 14 c.c. corresponds to 0·091 grm. KCy, indicating a strength of 0·455 per cent.

After the disappearance of the colour with phenolphthalein, the solution still appeared alkaline to methyl-orange. In the titration with half-normal acid described above, it was found that an additional 0·1 c.c. (in all 1·45 c.c.) was necessary to complete the reaction when a drop of methyl-orange was added to the colourless liquid. This corresponds to 0·047 grm. KCy, or 0·47 per cent, as against 0·45 per cent theoretical.

In the titration with decinormal hydrochloric acid, the end-point with methyl-orange as indicator was obtained with 15·2 and 15·1 c.c. respectively, thus indicating a percentage of 0·472 against 0·455 per cent theoretical. The higher values obtained with methyl-orange as indicator are due, as will be shown later, to a small quantity of carbonate existing in the alkaline cyanide.

In March, 1894, some experiments were undertaken by the writer to devise a method of estimating the amount of caustic alkali in cyanide solutions. It was found that when nitrate of silver is added to the solution in sufficient quantity to produce a permanent turbidity, the alkalinity may be rapidly and accurately estimated by titrating the slightly turbid solution with hydrochloric acid, using phenolphthalein as indicator. The double cyanide of silver and an alkali metal formed by the addition of silver nitrate to the alkaline cyanide is not alkaline to phenolphthalein. This was verified by the following experiments:—

a. A mixture was made consisting of 10 c.c., 0·53 per cent, potassium cyanide, and 10 c.c. of a solution of sodium hydrate, of which 1 c.c. was equivalent to 0·945 c.c. normal hydrochloric acid.

This mixture was first titrated with silver nitrate, 5·3 c.c. of the standard solution being required to produce a permanent turbidity. The silver nitrate solution was of such a strength that 1 c.c. = 0·01 grm. KCy. A drop of phenolphthalein was added, and the liquid titrated with normal hydrochloric acid. It was found that 9·4 c.c. were required (theoretical 9·45 c.c.).

b. 20 c.c. of 0·535 per cent cyanide solution were taken.

Silver nitrate was added in sufficient quantity to just produce a turbidity. The liquid was then titrated with decinormal hydrochloric acid, and phenolphthalein indicator. The quantity required was 2·5 c.c. N/10 hydrochloric acid. The colour of the indicator disappeared rather slowly towards the end of the reaction. This quantity (2·5 c.c.) may be taken to represent the amount of alkali (hydrate and carbonate) present in 20 c.c. of the solution of commercial cyanide used in this and the following experiments. It must be remembered that in titrating a carbonate with phenolphthalein as indicator, the value obtained represents the quantity of acid required to convert the carbonate into bicarbonate, corresponding to the equation—

$$K_2CO_3 + HCl = KCl + KHCO_3,$$

whereas with methyl-orange the number represents the quantity of acid required to convert the carbonate into chloride (*i.e.*, twice the quantity required with phenolphthalein) as follows:—

$$K_2CO_3 + 2HCl = 2KCl + CO_2 + H_2O.$$

c. A mixture was made of 20 c.c. of the same 0·535 per cent cyanide solution, and 10 c.c. decinormal caustic potash solution.

This was titrated first with silver nitrate, 10·95 c.c. being required to give a permanent turbidity. A few drops of phenolphthalein were added, and the solution titrated with N/10 hydrochloric acid. 12·65 c.c. of the latter were required. Subtracting the 2·5 c.c. corresponding with the alkali present in the cyanide, we have 10·15 c.c. (by theory 10 c.c.) representing the alkalinity of the caustic potash.

Addition of silver nitrate in excess of the amount required to give a permanent turbidity did not appear to affect the result, except in so far that the dense white precipitate of silver cyanide obscured the end-point of the colour reaction.

a. A mixture was made of 20 c.c., 0·535 per cent, potassium cyanide, and 10 c.c. decinormal caustic potash.

To this, 20 c.c. of the standard silver nitrate solution were added (*i.e.*, more than sufficient to convert KCy into $KAgCy_2$, but not sufficient to precipitate all the cyanogen as AgCy.

This mixture was titrated with N/10 hydrochloric acid, and phenolphthalein indicator. 12·55 c.c. were required.

Deducting 2·5 c.c. as before, we have 10·05 c.c. (against 10 c.c. theoretical) representing the alkalinity of the caustic potash.

b. A mixture was made of 20 c.c., 0·535 per cent, potassium cyanide, and 10 c.c. decinormal caustic potash.

To this, 25 c.c. of the standard silver nitrate was added (*i.e.*, more than sufficient to convert the whole of the cyanogen into AgCy). The precipitate was very dense and brown from presence of silver oxide, formed by the action of the caustic potash on the excess of silver nitrate. During the subsequent titration this brown tint disappeared, but towards the end of the reaction was succeeded by a purplish tint, which made the final point difficult to observe. It was found that 12·2 c.c. of N/10 hydrochloric acid were required to destroy the phenolphthalein colour. Deducting 2·5, we have 9·7 c.c. (against 10 c.c.) indicating the alkalinity of the caustic potash.

It is noteworthy that the presence of caustic alkalis, or the addition of the same to the cyanide solution before titration, does not affect the accuracy of the estimation of cyanide by means of silver nitrate. Moreover, the turbidity produced by the silver cyanide is not removed by the addition of moderate quantities of alkaline hydrate of ordinary strength.

When alkaline carbonates are present, they may be estimated as follows:—The solution is titrated with hydrochloric acid, using methyl-orange as indicator. The number obtained is the equivalent of the total alkali present (whether as cyanide, carbonate, or hydrate). The quantity of cyanide may be estimated in another portion of the solution by titration with silver nitrate, and its equivalent in hydrochloric acid deducted from the value obtained by the first titration. After the estimation of the cyanide as above, the same portion of solution may be titrated with N/10 hydrochloric acid, using phenolphthalein as indicator.

Methyl orange cannot be used for this purpose, as the turbidity masks the delicate change of tint, marking the end of the reaction.

The indication with phenolphthalein gives the equivalent in hydrochloric acid of the hydrate + half the carbonate (see above).

These results were confirmed by the following experiments:—

a. A solution of potassium carbonate was prepared such that 100 c.c. required 9·7 c.c. normal hydrochloric acid to produce neutrality with methyl-orange as indicator. A solution of potassium cyanide was prepared containing 0·53 per cent. It was found that 100 c.c. of this solution required 10 c.c. of normal hydrochloric acid to give the indication with methyl-orange.

The following mixture was made:—10 c.c. of the above cyanide solution, and 50 c.c. of the above potassium carbonate solution.

On titrating the mixed solution with normal hydrochloric acid, it was found that 5·8 c.c. were necessary to give the methyl-orange indication (by theory 5·85).

b. The following mixture was made:—10 c.c. of the above cyanide solution, 50 c.c. of the above carbonate solution, and 10 c.c. of a solution of caustic soda such that 10 c.c. = 9·6 c.c. normal hydrochloric acid.

This was titrated with normal hydrochloric acid, using methyl-orange as indicator. It was found that 15·5 c.c. were necessary. By theory:—

Equivalent of cyanide .. .. = 1·0 c.c.
,, potassium carbonate . = 4·85 ,,
,, caustic soda .. .. = 9·6 ,,

Sum of equivalents .. .. = 15·45 ,,

c. The following solutions were prepared:—

Potassium Cyanide, 0·455 *per cent.*—Hydrochloric acid equivalent of 10 c.c. with phenolphthalein = 6·75 c.c. N/10 HCl; with methyl-orange = 7·25 c.c. N/10 HCl.

Sodium Hydrate.—Hydrochloric acid equivalent of 10 c.c. with phenolphthalein = 9·1 c.c. N/10 HCl; with methyl-orange = 9·45 c.c. N/10 HCl (the difference being due to carbonate present in the solution).

Sodium Carbonate.—Hydrochloric acid equivalent of 10 c.c. with phenolphthalein = 5·15 c.c.; with methyl-orange = 10·35 c.c.

A mixture was made containing 200 c.c. of the above potassium cyanide, 10 c.c. of the above sodium hydrate, and 10 c.c. of the above sodium carbonate.

Calculating from the above values, 10 c.c. of the mixture should be equivalent, with phenolphthalein, to 6·8 c.c. N/10 hydrochloric acid; with methyl-orange, to 7·5 c.c. N/10 hydrochloric acid.

20 c.c. of the mixture were titrated with decinormal hydrochloric acid. The indication with phenolphthalein (which was observed with some difficulty) was obtained at 13·5 c.c. (theoretical = 13·6 c.c.). On adding methyl-orange and continuing the titration, the end-point was reached with 15·2 c.c. (theoretical 15 c.c.).

d. The following solutions were prepared:—

Potassium Cyanide, 0·548 *per cent.*—When this solution was titrated with N/10 hydrochloric acid, with phenolphthalein indicator, after addition of silver nitrate to produce a permanent turbidity, 1·25 c.c. of acid were required for every 10 c.c. of the cyanide solution indicating alkaline hydrates or carbonates.

Potassium Hydrate.—10 c.c. = 9·9 c.c. N/10 HCl, with phenolphthalein indicator.

Potassium Carbonate.—10 c.c. = 4·1 c.c. N/10 hydrochloric acid, with phenolphthalein indicator.

The following mixture was made:—20 c.c. of the above cyanide solution, 10 c.c. of the above potassium hydrate solution, and 10 c.c. of the above potassium carbonate solution.

This was first titrated with silver nitrate, 10·95 c.c. being required to produce a permanent turbidity. A few drops of phenolphthalein indicator were then added, and the titration continued with N/10 hydrochloric acid, of which 16·4 c.c. were necessary to complete the reaction. By theory:—

20 c.c. of the cyanide .. .. = 2·5 c.c. N/10 HCl.
10 ,, hydrate .. .. = 9·9 ,, ,,
10 ,, carbonate .. = 4·1 ,, ,,

Sum of equivalents .. = 16·5 ,, ,,

The above experiments are sufficient to show that the amount of cyanide, hydrate, and carbonate in a given solution may be estimated, with enough accuracy for practical purposes, from the three following determinations, each of which is rapidly made without demanding any special degree of skill or technical knowledge on the part of the operator.

1. Estimation of the cyanide by direct titration with silver nitrate.
2. Estimation of hydrate + half the carbonate by adding phenolphthalein to the same solution and continuing the titration with hydrochloric acid.
3. Estimation of total alkali by direct titration with hydrochloric acid, using methyl-orange as indicator.

The writer has great pleasure in acknowledging his indebtedness to his friend Clarence A. Seyler, B.Sc., for valuable assistance and suggestions in devising and executing the experiments described above; and to Dr. Morgan, Public Analyst, Swansea, for kindly allowing the use of his laboratory for carrying out these researches.

Royal Institution.—The Right Hon. Lord Rayleigh, F.R.S., Professor of Natural Philosophy in the Royal Institution, will deliver a course of six experimental lectures on "Waves and Vibrations" at the Royal Institution, on Saturdays, March 2, 9, 16, 23, 30, and April 6. His Lordship will also deliver the Friday Evening Discourse on April 5th, when his subject will be "Argon: the New Constituent of the Atmosphere."

REMARK ON THE RESEARCH OF CURTIUS AND DADICHEN: "SYNTHESES OF BENZENEHYDRAZINES BY MEANS OF HYDRAZINHYDRATE."

By A. PURGOTTI.

In the above-named memoir, received by the editor of this Journal on July 25 and published on September 15, the authors, along with other researches, made known their observations on the action of hydrazinhydrate upon 1, 2, 4-chlordinitrobenzene and 1, 2, 4, 6-chlortrinitrobenzene, and described the 1, 2, 4-dinitrophenylhydrazin as well as the 1, 2, 4, 6-trinitrophenylhydrazin along with some derivatives.

The authors above named were doubtless not acquainted with my first preliminary communication "Sull' azione dell' idrato d'idrazina sul chloruro di picrila" ("On the Action of Hydrazin upon Hydrazinhydrate upon Picryl Chloride"), which had been sent to the editor of the *Gazetta Chimica Italiana* on December 29, 1893, and was published on March 15, 1894. In that communication I described the 1, 2, 4, 6-trinitrophenylhydrazin, and reserved to myself to publish further results on the same question and on the chlornitrobenzene. In like manner Curtius and Dadichen have not been aware of my memoir "Sulla 2, 4-dinitrofenilidrazina a sulla picril-idrazina a loro derivati" ("On 2, 4-Dinitrophenylhydrazin and on Picrylhydrazin and their Derivatives"), which were sent in to the *Gazetta Chemica Italiana* on May 9, was announced in the issue for the same month, and was published July 4 of that year.

In this research I arrived at the same conclusions as Curtius and Dadichen, and among the various derivatives I described the condensation product of picrylhydrazin with acetacetic ester—a product which the above authors have not obtained.

From the above dates the priority of the synthesis of 1, 2, 4-dinitrophenylhydrazin and of 1, 2, 4, 6-trinitrophenylhydrazin by means of hydrazinhydrate is manifest. —*Journal für Praktische Chemie*, N.S., li., Part 1 and 2, p. 111.

ON THE FORMATION OF HYDRAZIN IN AN INORGANIC MANNER.

By P. DUDEN.

Since the discovery of hydrazin by Curtius and Jay in 1889, a series of methods for obtaining this interesting product have been published by them, as well as by Thiele and Von Pechmann.

All these methods have the common feature that they take a circuitous way through nitrogenous organic substances. They set out from such aliphatic carbon compounds as contain a diazo-nitrosamin or nitramin group, combined with a carbon-complex which may be easily split off. The formation of hydrazin is effected either by direct reduction or by reduction followed by the hydrolytic scission of the primary amido-product formed.

Attempts have been made to transfer this reaction to the inorganic region or to arrive at hydrazin by proceeding from simple purely inorganic nitrogen compounds. It appears, however, that the nearest attempts, such as the reduction of nascent nitrogen or nitrous oxide, or the catenation of the amido-groups of hydroxylamine and ammonia, or the use of metallic ammonium compounds containing an amido-group, do not lead to the desired end.

On the contrary, I have made some experiments with the potassium salts discovered by Fremy and more closely examined by Raschig, and arising on the reaction of sulphurous acid with potassium nitrite. I have observed that nitric oxide potassium sulphite, $K_2SO_3N_2O_2$, on cautious reduction in an alkaline solution, yields hydrazin. Hence by means of this purely inorganic salt it is possible to transmit nitrogen into hydrazin.

This salt, discovered by Davy, has been examined some years ago by Divers and Haga (*Journ. Chem. Soc.*, 1885) as to its behaviour with reductive agents. According to their observations, by reduction with sodium amalgam in a concentrated alkaline liquid it is substantially converted into potassium hyponitrite and potassium sulphite according to the equation—

$$SO_3KN_2O_2 + H_2 = SO_3KH + 2KNO.$$

There is a simultaneous formation of hydroxylamine and ammonia.

If this reduction is effected in the cold with sodium amalgam or zinc powder and ammonia (or soda-lye), we obtain a strongly reductive solution which after acidulalation contains a hydrazin salt. There is therefore formed along with hyponitrite the reductive product corresponding to nitric-oxide potassium sulphite, the formation of which, according to Raschig's formula, may be shown as—

$$\begin{matrix}KSO_3\\KO\end{matrix}{>}N.NO + H_6 = \begin{matrix}KSO_3\\H\end{matrix}{>}N.NH_2 + H_2O + KOH =$$
$$= H_2N.NH_2 + K_2SO_4.$$

The intermediate product first formed could not be more closely examined, as on shaking up with benzaldehyd it yields no sparingly soluble benzaldehyd compound.

In effecting this reaction the nitric oxide freshly prepared is suspended in ice-water, and whilst being refrigerated it is gradually mixed with amalgam in slight excess until a specimen of the liquid strongly reduces Fehling's liquid, and after acidulation and heating, benzalazin separates out on the addition of benzaldehyd. The product thus obtained, $C_{14}H_{12}N_2$, melts at 93°, and has the properties and composition of benzalazin.

With sulphuric acid it yields hydrazin sulphate at 256°. Instead of amalgam we may use other reductive agents acting in alkaline solutions. The production of hydrazin is not sharp, as other reduction products are formed simultaneously.—*Berichte*, xxvii., p. 3498.

THE ACTION OF ALKALIS UPON ORTHONITROPHENYLHYDRAZIN.

By E. NIETZKI and E. BRAUNSCHWEIG.

Some years ago one of the present writers attempted to obtain hydrazin from a nitrised phenylhydrazin. The material used was orthonitrophenylhydrazin sulph-acid.

On boiling with alkali-lye it evolved not a trace of hydrazin, and the experiments were abandoned. Dr. Grandmougin, however, who had arrived at a similar negative result, sent us a specimen of a finely crystalline body which he had obtained on supersaturating the aniline liquid with an acid.

As the examination of the present sulpho-acid gave no insight into the constitution of the compound which evidently belonged to a new class of substances, we endeavoured to obtain the simplest representative of this class, and used as our initial material Bischler's orthonitrophenylhydrazin.

Azimidal.—Orthonitrophenylhydrazin if heated is very quickly attacked by alkaline-lyes, and even by aqueous ammonia. It dissolves, the liquid becomes nearly decolourised, and on supersaturation with an acid the product of the reaction separates out in needles nearly colourless. On crystallisation from dilute alcohol the new substance is obtained pure, of the composition $C_6H_5N_3O$, having the melting-point 157°. It had been formed by the elimination of water from nitrophenylhydrazin. It has the properties of a somewhat powerful acid. It forms with alkalis salts easily soluble, but with alkaline earths and the heavy metals salts which are in general more sparingly soluble. The lead salt—

$$(C_6H_4N_3O)_2Pb$$

crystallises very readily. If crystallised from hot water it forms colourless shining leaflets which deflagrate at 270°.

It is characterised by great stability and slight tendency to reactions. Acetic anhydride is without action. Nor is it attacked by reductive agents, a proof that the nitro-group is not present as such.

Iodethyl has no action even at a rather high temperature. On heating the lead salt with this reagent in a closed tube, there was at first no result, but a reaction set in when the temperature was raised to 180°. The contents of the tube were coloured brown by the liberation of iodine. They were diluted with alcohol and separated from lead iodide. On evaporating the solution there appeared dark shining crystals of a metallic lustre.

The substance had a strong odour of iodine, gave off violet vapours at a gentle heat, and displayed all the properties of the periodides often obtained from the iodides of the ammonium bases. The iodide was converted into a chloride by treating the alcoholic solution with precipitated silver chloride. The chloride is very soluble both in water and alcohol. It does not crystallise and therefore the platinum double salt was prepared. It forms a yellow crystalline precipitate, $(C_{10}H_{14}N_3Cl)_2PtCl_4$, a remarkable instance of a salt free from oxygen. The new base must have arisen from the original compound by the exit of an atom of oxygen and the introduction of two ethyl groups. All the properties of the base show the presence of a quaternary ammonium group.

If we take away from a chloride of the formula $C_{10}H_{14}N_3Cl$ (as in the double platinum salt) one molecule of ethyl chloride and another ethyl group, we arrive at a compound $C_6H_5N_3$. Such is Ladenburg's azimidobenzol,

If the new substance is a derivative of azimidobenzol. we may conjecture that it may be formed by ethylisation. Azimidobenzol, obtained according to Ladenburg's directions from orthophenylendiamine, was heated to 150° in a sealed tube with iodethyl and one molecule sodium ethylate.

If the alcoholic solution of the product of the reaction is mixed with solution of iodine, crystals are separated which have the appearance and behaviour of the periodide above mentioned, and after being freed from iodine yield a platinum double salt as above described.

Hence a derivative of azimide was formed from the substance just described with a removal of oxygen.

Evidently the original substance in view of its properties and formation must be a hydroxyl derivative. We propose for substances of this class the name of "azimidoles."

As the hydrogen of these bodies is easily replaced by metals, we may understand that on exchanging them for hydroxyl substances of strongly acid properties are formed.

A subsequent analysis of the above-mentioned periodide shows that it contains no oxygen.

If nitrohydrazinsulph-acid is heated with an excess of soda-lye, it congeals on cooling to a paste of colourless needles, a bi-sodium salt, $C_6H_3N_3Na_2SO_4 + H_2O$.

Azimidosulph-acid is hence bibasic.—*Berichte*, xxvii., p. 3381.

Royal Victoria Hall, Waterloo Road, S.E.—At the British Association last autumn, much excitement was caused by the announcement that Lord Rayleigh and Prof. Ramsay had discovered a new element in the air. Their investigations will form the subject of one of the well-known popular lectures at the Royal Victoria Hall, on Tuesday, February 26, at 8.30. It is a "sign of the times" that the newest scientific discoveries are expounded to the public at an admission fee of one penny.

THE SECRET OF THE BROWNIAN MOVEMENTS.*

By R. MEADE BACHE.

(Continued from p. 84).

Heat I applied in various ways, either irregularly or in an endeavour to distribute it as equally as possible on the glass slide on which the particular experiment was made. Mere currents are set up during the adjustment of temperature from radiation. At the same time one can observe and differentiate the motions due to the brownian movements, the motions along currents, and also the motions from terrestrial gravity, if any, exhibited by particles, if the specific gravity of the substance be great, and the microscope be set at an angle with the vertical.

Cold I also applied, putting the slides with their cover-glasses in a freezing mixture of broken ice and water, and reducing them to a very low temperature. Still the movements went on as apparently unmodified as ever. Herr Exner says it will be remembered that glycerin, which under ordinary conditions shows absolutely none or almost no molecular movement, shows it clearly when warmed up to the temperature of 50° C. In all the finely divided bodies, however, which I examined, there seemed to be no increase or diminution in the intensity of the movements, corresponding with their alternate subjection to heat and cold. There were occasions in which I thought that I observed acceleration from light, but I always ended by imputing it to the force of imagination, and if it were not justly ascribable to that cause, the fact that it could be so ascribed is proof positive that if, through the influence of light and heat, any intensification of the movements of the particles took place, it must have been very small. Moreover, the evidence is certainly here to show that even if the movement were intensified by light or heat, that was the only influence that could be ascribed to them, that light and heat could not be deemed the cause of the movement. And lastly, Herr Wiener's micrometric measurements of the range of movement at different temperatures completely bore out this conclusion.

The theory of Herr Wiener that the movements are due to the action of the red wave of light and heat is refuted by the single fact that, as I have proved by experiment, one may interpose at pleasure between the source of light or heat and the particles either a violet glass or a red glass without being able to observe the slightest alteration in the movements, either as to their range or their velocity. That is to say, red rays may be either partially excluded or selectively admitted without diminishing or increasing the liveliness of movement. Hence light can have nothing to do with the phenomenon under discussion, and I have just shown, through the citation of the freezing mixture experiment, that heat can have nothing to do with it.

I have reserved to the very last the discussion of the question as to whether or not the shock, if any there be, from evaporation can have anything to do with the movements, although this was a point that entered into my first investigations. I have reserved it to the last, because its discussion requires more than the brief space which I have devoted to the previous individual results, and because it leads directly to the conclusion that I have finally reached as to the true cause of the movements. I started out with the conception, which it seems is common to everyone, that evaporation might be accompanied with a series of minute explosions, which produce shocks that manifest themselves through the mass of an aqueous solution in the form of minute movements of finely divided matter held in unstable equilibrium by suspension

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* Read before the American Philosophical Society, April 20, 1894. —From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

in the fluid, and that these, escaping cognisance from any ordinary observation, might be visible as such, or in their effects, through the instrumentality of high powers of the microscope. I had come to believe long before, from observation and experiment, that no tremors from mechanical agency or any other, except perhaps from evaporation, could produce the peculiar movements known as brownian, and finally it remained to discover if this or any other intrinsic cause were at work that would account for them.

At this point I encountered an obstacle. My high powers of the microscope were both water-immersion lenses. It seemed, therefore, that even when I had had the drop of liquid under observation, sealed beneath a cover-glass, I might have included, by the use of the water-immersion lens itself, an evaporating surface which might have produced the optical illusion of the movement of the particles in suspension. I proceeded, however, with my experiments upon the assumption that this, as the event proved to be the case, was not true, and meanwhile procured from Vienna a one-fifteenth dry-lens by Reichert, the highest power of dry-lens that he makes.

I had already obtained for high-power lenses a film of liquid thin enough to be observed through all its strata, free of air within the cell, and protected from evaporation by being hermetically sealed. Any ordinary manufactured cell is too deep, and with all precautions taken contains a little air. On the other hand, the mere cover-glass superposed on a glass slide contains too slight a depth of fluid. I made a cell by using gum-shellac traced in a circlet on a glass slide, which cell, when partially dried, is filled to the brim with the liquid to be observed upon, whereupon the cover-glass is pressed into the yielding gum, thereby expressing the contained air with the superfluous liquid, when the product, dried over night, is fit for use on the following evening. One slide, prepared in this manner and filled with a slightly tinted solution of carmine from cochineal, had been observed upon by me for weeks, with a one-tenth water-immersion lens, and afterwards, upon the arrival of the one-fifteenth dry-lens, was observed upon without showing any variation in the range and vividness of movement of the particles subjected to examination. I have even covered the whole microscope with a pall of thick black woollen cloth, so that not a ray of light could enter it either through the cover-glass or the eye-piece, and then carefully placing the eye close to the eye-piece, have suddenly thrown light upon the cover-glass, when the brownian movement among the particles was perceived in as active play as ever. I have therefore concluded from all these experiments that neither heat nor light, nor electricity, nor magnetism, nor mechanical shock, nor, finally, evaporation, is operative in producing the movements; in a word, that the particles move uninfluenced by these forces. I am therefore constrained to believe, upon the basis of the information that I have obtained in the manner described, that it is not the particles which are moved by their own energy, or moved by any energy directly imparted to them from outside sources, but that it is the fluid that moves them.

If their own energy moves the particles, we should see them at the same time obedient also to the law of gravitation among themselves, manifested as the resultant of whatever forces are in play, whereas, although they must be obedient to the law of gravitation among themselves, its effects, and generally as well those of terrestrial gravity, are so masked as not to be at all perceptible. Now when we consider how minute all of these particles are, and yet that they move apparently unhindered with such constancy and force, it ought to be apparent, I should think, that they have no self-motive power. However erratic the paths of individual particles may be, the likeness among the movements is extraordinary, so almost identical in every case, varying in greatness of range and rapidity only in inverse ratio to the size of the particle, that we cannot conceive of self-actuated particles so behaving; for relative greatness of size in self-actuated particles ought to coincide with relatively greater, not relatively less, energy of movement; whereas here the case is reversed. But there are other facts that I have observed through experiment which also prove what I say. In alcohol and, as far as my experiments go, in fixed and volatile oils, the brownian movements are not observable, and yet the microscope plainly reveals that the movements of foreign bodies in all these is as free as in aqueous solutions, and I think more so. So molecular movements of solid particles in suspension in aqueous fluids must take place perforce of the constant repulsions of the constituent molecules of the particular liquid present—water. The minute drops of oils supernatant on water, some of them no larger than the particles in the water below, observed by Dr. Brown, as he says, to be almost or wholly motionless, so behave because the molecules of water glide by the molecules of a substance for which they have not even the affinity that would compass opposition. Be the globules of oil on water never so small or large, the molecules of the aqueous fluid glide by them. Whether a small or a large globule of oil be the particle itself on water, there is no movement of the particle. Dr. Brown says none, or almost none. I think that he was mistaken, that there is no molecular movement whatever.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 7th, 1895.

Dr. Armstrong, President, in the Chair.

Messrs. W. Herbert Walden, Robert H. Wilson, and J. Young were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Eugen Blume, Russell Ho., Trinity, Edinburgh; Virgil Coblentz, Ph.D., M.A., 115 W. 68th Street, New York, U.S.A.; John Francis Hutchins Gibbard, 362, Mare Street, Hackney; Alexander Gunn, 66, Finsbury Park Road, N.; Evan Lewis Jones, B.A., 4, Bank Buildings, Llandilo; John McGlashan, Cawnpore Sugar Works, Cawnpore, India; Lama Gray Patterson, Washington, Pa., U.S.A.; Thomas Coke Squance, M.D., M.S., &c., 4, Beauclerc Terrace, Sunderland; Alfred F. Theodosius, B.A., Magdalen College School, Oxford; George John Ward, The Cottage, Hallam Fields, Ilkeston.

Of the following papers those marked * were read:—

*12. "*The Action of Heat on Ethylic β-amidocrotonate.*" Part II. By J. Norman Collie, Ph.D.

In Part I. of this paper the author has shown that when ethylic β-amidocrotonate is heated it condenses to form a pyridine derivative, ethylic lutidone-monocarboxylate. He has since found that at least three other nitrogenous condensation products are formed when the amidocrotonate is destructively distilled.

The compound which is formed in largest quantity is ethoxylutidine (αγ-dimethyl-α′-ethoxypyridine),

$$2C_6H_{11}NO_2 = C_9H_{13}NO + NH_3 + CO + CO_2 + C_2H_4.$$

It is a pleasant-smelling liquid, b.-p. 217—218° (corr.). It forms a platinum salt, which melts at 226° (corr.) with much decomposition. When heated in a sealed tube with fuming hydriodic acid, ethylic iodide and pseudolutidostyril are produced.

A dimethylpyrrol is also formed in small quantities,—

$$2C_6H_{11}NO_2 = C_6H_9N + 2CO_2 + 2C_2H_4 + NH_3 + H_2.$$

This dimethylpyrrol seems to be identical with one which was obtained by Ciamician and Wiedel by destructively distilling gelatin. Its boiling point lies between 170°

and 175°. It has also been obtained by Knorr by reducing isonitroso-ethylic β amidocrotonate.

A third substance has been isolated which is also doubtless a pyridine derivative. It is produced by the following reaction:—

$$2C_6H_{11}NO_2 = C_6H_8N_2O + EtOH + CH_3COOEt.$$

When heated with zinc-dust, it gives α-picoline. It contains a hydroxyl group, for it yields a monochloride with pentachloride of phosphorus. It is probably either α-methyl-γ-amido-α'-hydroxypyridine or α-methyl-α'-amido-γ-hydroxypyridine. It does not diazotise when acted on with fuming hydrochloric acid and sodium nitrite, but with nitrous fumes in aqueous solution it forms a curious addition product:—

$$C_6H_8N_2O + NO_2 + H_2O = C_6H_{10}N_3O_4.$$

*13. "*The Acidimetry of Hydrogen Fluoride.*" By T. Haga and Y. Osaka.

The authors have separately examined the behaviour of the usual indicators in the neutralisation of hydrofluoric acid. That its alkali salts blue litmus, and that its avidity number places it among the vegetable acids rather than with the strong mineral acids, appear to be the only two facts yet recorded bearing upon its acidimetry.

To get uniform indications it was found necessary to have not only the acid pure, but the titrating solutions also; a little silica, alumina, or carbon dioxide affecting the titration more than it would in the case of the ordinary mineral acids.

Pheuolphthaleïn is the best indicator, and leaves nothing to be desired when potash or soda is used for the titration. *Rosolic acid* is almost equal to it, and can be used besides with ammonia. With both indicators the change of colour has the advantage of being very evident in platinum vessels.

Both *cochineal* and *brazil-wood* infusions give satisfactory results. Brazil-wood paper shows alkalinity before all the acid is neutralised, and cannot, therefore, be used. *Turmeric paper* gives fairly good results. *Methyl orange* is useless.

Litmus, *lacmoïd*, and *phenacetolin* are all capable of being made to yield accurate results in the hands of an experienced person. Some peculiarities in the behaviour of litmus are described in the paper which suggest the conclusion that the molecule of hydrogen fluoride may be H_3F_3 or H_4F_4.

*14. "*Composition of Ancient Silver Ornaments from Peru.*" By Miss C. Walker.

The two ornaments examined were found in the ancient graves of Incas, at Chimbote, and they were analysed in the Chemical Laboratory of the University of Virginia. Both ornaments were covered by a thin crust, chiefly composed of silver chloride and a basic copper carbonate in the one case, and of cuprous oxide in the other. One ornament was a silver plate composed of 85·24 per cent of silver, 13·96 per cent of copper, and 0·15 per cent of gold. The other ornament was a ring, joined by soldering the ends of a flat metallic band. This consisted of 25·51 per cent of silver, 72·09 per cent of copper, 0·25 per cent of gold, 1·21 per cent of iron, 0·5 per cent of zinc, and about 0·1 per cent of lead. The iron, lead, and zinc were probably derived from the solder.

It would seem that these ornaments had been made from native silver.

*15. "*Molecular Change in a Silver Amalgam.*" By Miss F. T. Littleton.

When an amalgam of silver and mercury is moderately heated, considerable swelling takes place, suggestive of the escape of gas, and, on cooling, the pasty mass sets to a hard crystalline porous substance. The increase in volume is most considerable when the metals in the amalgam are present in the proportions corresponding with the formula $AgHg_4$.

On examining the action it is found that no appreciable quantity of gas escapes from the amalgam, and the swelling must therefore be attributed to the molecular changes which accompany the union of the two metals.

16. "*Sulphocamphylic Acid.*" II. By W. H. Perkin, jun.

At the commencement of this investigation in 1891 a number of analyses of sulphocamphylic acid were carried out, as mentioned in the previous communication (*Proc.*, 1893-94, p. 110), and the author then observed that at a temperature of 110—115° this acid has the composition $C_9H_{14}SO_5$ or $C_8H_{12}(SO_3H)\cdot COOH$, the crystals of the acid which separate from aqueous solution being $C_9H_{14}SO_5 + 3H_2O$; this observation has since been confirmed by Koenigs and Meyer (*Ber.*, 1894, 3466).

That this formula correctly represents the composition of sulphocamphylic acid is shown by the analysis of its sulphobromide, $C_8H_{12}(SO_2Br)\cdot COOH$, which the author has succeeded in preparing by the interaction of the potassium salt of the acid and phosphorus pentabromide. This derivative crystallises from dilute methyl alcohol in prisms; it melts at 152°, and at a slightly higher temperature decomposes, evolving sulphur dioxide. By extracting the black residue with light petroleum, and re-crystallising the product from formic acid, a colourless crystalline acid, $C_8H_{12}Br\cdot COOH$, is obtained—

$$= C_8H_{12}(SO_2Br)\cdot COOH - SO_2.$$

This new acid melts at 130°—132°, and is readily acted on by alcoholic potash, being converted into an acid of the composition $C_8H_{11}\cdot COOH = C_8H_{12}Br\cdot COOH - HBr$. This acid, which melts at about 105°, may possibly be identical with the acid of this composition (m.-p. 108°), which is formed when sulphocamphylic acid is fused with soda (see below).

The author has continued his experiments on the fusion of sulphocamphylic acid with potash and soda, and finds that in all cases the product contains two isomeric unsaturated acids, $C_8H_{11}\cdot COOH$ (m.-p. 108° and 148), which can be separated only with great difficulty by re-crystallisation, but which were finally obtained in a pure condition by taking advantage of the fact that the aqueous solution of the ammonium salt of the higher melting acid dissociates readily at 80°, the acid separating, whereas the ammonium salt of the acid of melting-point 108° remains unchanged at this temperature.

The acid melting at 148° has already been obtained by Kachler (*Annalen*, clxix., 133); it is readily acted on by bromine, hydrogen bromide being evolved, and is converted into a crystalline acid, $C_8H_{10}Br_3\cdot COOH$, which melts at 178°.

The isomeric acid melting at 108° is also readily attacked by bromine, but no hydrogen bromide is evolved, and it yields, on oxidation with permanganate, a syrupy hydroxy-acid.

A careful investigation of these new compounds, as well as of those mentioned in the previous communication, is in progress.

17. "*Derivatives of Ethyl-orthotoluidine.*" By W. MacCallum, jun.

This paper contains an account of work conducted in the year 1893, at Mülhausen, by the late Mr. William MacCallum, jun. The account now given has been drawn up from Mr. MacCallum's notes by Dr. Hepburn. The object of the investigation was to ascertain whether nitrosoethyltoluidine and the diazoamido-derivatives of nitroethyltoluidine could be converted into ethylisindazole and nitroethylisindazole respectively. This proved not to be the case, but in the course of the investigation several new compounds were prepared, amongst them being *nitroethylorthotoluidine*, *ethyl toluylenediamine*, *nitroethylacetoorthotoluidine*, m-*nitroethylnitrosoorthotoluidine* and *ethyldiazoamidotoluene*. The last-named compound furnishes the same nitro-indazole as is formed by diazotising *m*-nitrotoluidine and heating the product with dilute sulphuric acid.

18. "*Acetyl Derivatives of Benzaconine and Aconitine.*" By Wyndham R. Dunstan, F.R.S., and Francis H. Carr.

The authors have made a number of experiments in the hope of being able to convert benzaconine into aconotine by introducing an acetyl group into it. These experiments have so far been unsuccessful, but several new compounds have been obtained, both from benzaconine and from aconitine, the analyses of which serve to further confirm the formulæ which the authors have previously proposed for these alkaloids, $C_{31}H_{43}NO_{11}$ and $C_{33}H_{45}NO_{12}$, whilst the analytical results do not bear out the formulæ proposed by Freund and Beck, $C_{32}H_{45}NO_{10}$ and $C_{34}H_{47}NO_{11}$. By acting on benzaconine dissolved in chloroform with acetic anhydride during 24 hours at the ordinary temperature an amorphous base is obtained which forms crystalline salts; the *hydrobromide* melts at 265°. The substance does not seem to be toxic. When hydrolysed by heating with water in a closed tube it furnishes acetic acid and benzaconine.

At 100°, or by Liebermann's method, a crystalline base (m.-p. 255°—256°) results from the action of acetic anhydride. On hydrolysis this substance breaks up into aconine, benzoic acid, and 24·4 per cent of acetic acid, proving it to be a *triacetyl benzaconine.* This derivative appears to be identical with that described by Freund and Beck as a monacetyl derivative. These observers do not appear to have estimated the amount of acetic acid produced on hydrolysis, but to have trusted to the results of combustions, which, as the authors have previously pointed out, furnish by themselves no safe criteria of composition with such compounds. This base also appears to be non-poisonous.

Acetyl chloride, acting in the cold on benzaconine dissolved in chloroform, produces a crystalline base (m.-p. 162°), which forms crystalline salts, including an aurichloride. It also appears to be a *triacetyl benzaconine*, $C_{31}H_{40}(CH_3CO)_3NO_{11}$.

The further action of acetyl chloride on this substance, or on benzaconine, in a sealed tube at 100° C., results in the formation of a crystalline base (m.-p. 211), which appears to be *tetracetyl benzaconine.* It forms a remarkable colourless aurichlor-derivative (m.-p. 225°).

Acetic anhydride does not act on aconitine.

Acetyl chloride forms *diacetyl aconitine* (m.-p. 158°), which differs from its isomeride triacetyl benzaconine principally in its physiological action, which resembles that of aconitine, and also in the property of forming an aurichlor-derivative, as well as in its crystalline form.

Triacetyl aconitine (m. p. 206—207°) also differs from its isomeride tetracetyl benzaconine in its crystalline form and physiological activity.

Pyraconitine and acetyl chloride interact, forming a crystalline base (m. p. 203°), which is *triacetyl pyraconitine.* This substance does not seem to be poisonous. In determining the composition of each of these substances, reliance has been placed on the determination of the amount of acetic acid formed on hydrolysis. Combustions for carbon and hydrogen have also been made, and the results bear out the formula suggested by the authors for aconitine, and do not agree with the formula suggested by Freund and Beck, as will be seen from the following table, which also includes analysis of aconine and of pyraconitine hydrobromide.

		Freund.	Dunstan and Carr.	
		Calculated.	Found.	Calculated.
		$C_{40}H_{53}NO_{14}$.		$C_{39}H_{51}NO_{15}$.
Triacetyl aconitine,	C.. ..	62·25	60·42	60·54
	H.. ..	6·87	6·82	6·59
		$C_{38}H_{51}NO_{13}$.		$C_{37}H_{49}NO_{14}$.
Diacetyl aconitine,	C	62·55	60·98	60·74
	H.. ..	6·99	7·06	6·70
		$C_{32}H_{43}NO_9HBr$.		$C_{31}H_{41}NO_{10}$.
Pyraconitine hydrobromide,	C	57 65	55·8	55·69
	H.. ..	6·60	6·28	6·28
		$C_{25}H_{41}NO_9$.		$C_{24}H_{39}NO_{10}$.
Aconine,	C.. ..	60·12	57·31	57·48
	H.. ..	8·21	8·02	7·78

In establishing their new formula for benzaconine ($C_{31}H_{43}NO_{11}$) the authors relied on the determination showing that one molecular proportion of acetic acid is separated when it is formed from aconitine ($C_{33}H_{45}NO_{12}$). The base being amorphous did not lend itself well to the confirmation of this formula, especially as the composition of the alkaloid only differs within the limits of experimental error from that of aconitine. They showed, however, that the percentage of gold in the remarkable colourless aurichlorbenzaconine agrees well with the calculated number. Freund and Beck state that they have been unable to obtain this substance. The authors can only reply that they find no difficulty whatever in producing it, and that one of them, in conjunction with Mr. E. F. Harrison, has now succeeded in converting it into a crystalline aurichloride.

19. "*Aconitine Aurichlorides.*" By Wyndham R. Dunstan, F.R.S., and H. A. D. Jowett. B.Sc.

In a previous communication (*Trans.*, 1893) the authors described three modifications of aconitine aurichloride, differing in melting point and apparently in crystalline form, each being produced under different conditions from the amorphous aurichloride and convertible into each other. The α-compound (m. p. 135°) was obtained by crystallising from aqueous alcohol, aqueous acetone, or from a mixture of chloroform and ether; the β-compound (m. p. 152°) was formed by crystallising from strong alcohol, and the γ-compound (m. p. 176°) by crystallising the β-compound from a mixture of chloroform and ether.

Freund and Beck (*Ber.*, xxvii., 724) have stated that the α-aurichloride is really a trihydrate, and that the β-compound is the anhydrous salt; the γ-compound they do not mention. They describe a new salt which they state is an alcoholate, and is obtained by crystallising from absolute alcohol; this salt melts at 135°, and loses its alcohol when heated or left for a long time in the desiccator.

The authors have, therefore, again examined the aurichlorides, and have confirmed their previous results, The α-aurichloride cannot be regarded as a trihydrate, since it contains 19·64 per cent of gold, the formula—

$$C_{33}H_{45}NO_{12},HAuCl_4$$

requiring 19·89 per cent, or, using Freund's formula for aconitine, 19·93 per cent, whereas a trihydrate requires either 18·86 per cent or 18·89 per cent, depending on which formula is taken. On heating at 100—120° during many hours and weighing at intervals, the total loss was much less (2 per cent) than that required for the trihydrate, although the salt had slightly decomposed. After this prolonged heating, the substance still melted very close to its original point.

Moreover, they have now succeeded in producing the α-aurichloride in the absence of water by crystallising from anhydrous acetone.

The authors have also examined the substance which Freund and Beck regard as an alcoholate of aconitine aurichloride. The salt prepared by the method they describe closely resembled the β-aurichloride in appearance. The air-dried salt melted indefinitely between 145—152°, but (after drying at 100°) at 152°. By drying this substance under different conditions the authors find that the loss is variable, but in no case does it amount to the percentage required for an alcoholate—4·46 or 4·47 per cent. They conclude that this substance is merely the β-aurichloride with a small quantity of alcohol still adhering to it; this alcohol is slowly lost when the salt is exposed to air.

Anniversary Dinner.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Hotel Métropole on Wednesday, March 27th, at 6.30 for 7 p.m. It is hoped that as many Fellows as possible will be present.

Erratum.—In the report of the Chemical Society's meeting for Jan. 17th (p. 71, col. 2, five lines from bottom), the formula should read :—$C_{18}H_{30}O_{14}(N_2HC_6H_5)_2$.

NOTICES OF BOOKS.

Cellulose, an Outline of the Chemistry of the Structural Elements of Plants with reference to their Natural History and Industrial Uses. By Cross and Bevan (C. F. Cross, E. J. Bevan, and C. Beadle). London and New York: Longmans, Green, and Co. 1895. 8vo., pp. 320.

Sparingly reactive as are the celluloses, they yet present to the chemist problems of the greatest interest. We are therefore much indebted to the authors for having brought to a focus the results already reached concerning these compounds, and for indicating—as they do most carefully—how our knowledge of the celluloses may be extended and deepened. The study of their relations with the starches, gums, and sugar leaves room for much good work.

Perhaps still more interesting is the investigation of the celluloses to the physiologist who seeks to trace how these apparently inert bodies are evolved from the constituents of plant-food, and how they in turn are transmuted within the organism. It is interesting to note the existence of cellulose in animals. The authors here raise the question whether animal celluloses—tunicin, &c.,—are elaborated *de novo* in the Ascidia, or if they retain their constitutional features in passing from the vegetable to the animal organism (pp. 87 and 88).

Perhaps the technicist is especially concerned with the morphology, the physiology, and the embryology of cellulose. In the manufactures of textile goods, of paper, of gun-cotton, of various water-proof tissues, and in the arts of bleaching, dyeing, and tissue printing, we can lay no firm foundation without a rational study of plant-fibres. The way in which John Mercer succeeded in giving to cotton tinctorial properties approaching those of animal fibre was truly noteworthy. Still more noteworthy is the manner in which his discovery has been neglected under the most frivolous pretexts.

The authors first discuss the typical cellulose and its group, passing then to its natural compounds, the pecto-celluloses and muco-celluloses, as also the adipo-celluloses and cuto-celluloses. The second group have the characteristic property of forming gelatinous hydrates, approaching those of certain seeds and fruits. But the pectic group have less hydrogen in proportion to the carbon and oxygen than the carbohydrates.

Of the adipo-celluloses cork serves as the type.

The authors show that the elaboration of the compounds in question is, as regards "mass effect," the main work of the vegetable world. They are not aware of any special proof of the assumption that the celluloses are non-nitrogenous *ab initio*. It is at least possible that in the earlier stagss of growth they contain NH_2 residues. They show that the chemistry of the vegetable world, which depends in its proximate relationships upon the polyhydroxy-derivatives of the C_6 unit, is a most striking manifestation of the carbon atom itself.

The third part of the work is devoted to the experimental and applied part of the subject, and should not be entered upon by the student without a previous assimilation of the former parts. The authors give indications for the microscopic examination of the fibres. They recommend the student to sow some flax seed and examine the stem from time to time during the growth of the crop. Experiments are to be made in bleaching, using flax and jute as raw materials. Rapid combustion is to be studied, as also hydration and dehydration, and the effects of solvents, the parchmentising process, and destructive distillation. Next follow methods for the identification of the members of the group.

Bleaching processes are studied as applied to textiles and paper pulp. Under dyeing and printing processes we find a notice of what was until lately a matter of controversy,—the question whether dyeing is a mechanical or a chemical process. The authors regard it as a special case of the transfer of a body—*i.e.*, a tinctorial substance —from one solvent to another. Hence a dyed fibre is a solid solution of the colouring matter in the fibre substance. Attention is called to the "cosmopolitan relationships" of the ligno-celluloses as compared with the celluloses.

A suggestion is thrown out that laundry work should be more definitely organised as a chemical industry.

Notice is taken of the influence of papers, according to the raw material employed, on the permanence of books and documents. The nitro-celluloses, or rather cellulose nitrates, are next considered.

In summing up the authors tell us that the study of the celluloses "is a province of applied chemistry, whereas in many others the distinctions between science and practice exist only in the minds of those who grasp neither the one nor the other."

Had we the power we would have this sentence inscribed on high not only in every technical school but in every chemical works.

The work is enriched with fourteen microphotographs of various fibres.

Our opinion of the book is that it should be found on the bookshelves of every factory, laboratory, or office where fibrous materials are bought, sold, or elaborated.

The Cyanide Process for the Extraction of Gold, and its Practical Application on the Witwatersrand Gold Fields in South Africa. By M. Eissler. London: Crosby Lockwood and Son. 1895. Crown 8vo., pp. 90.

For the appearance of this useful work we are doubtless indebted to the recent litigation on the cyanide process. But we must not suppose that Mr. Eissler has written merely on the spur of the moment. He has spent some years at the South African gold fields, and has enjoyed especial opportunities for a close and practical study of the process. The solubility of gold when in a state of fine division was known, according to the author, "in the middle ages, and the gilding of metals was carried out in those remote days by jewellers and alchemists by the use of gold in cyanide solutions." Here we wish the author had been a little more explicit and informed us how the metallurgists of the past obtained their cyanide. Free cyanogen, according to all the text-books, was discovered by Gay-Lussac. Even Prussian blue and potassium ferrocyanide scarcely date back to the middle ages. But hydrocyanic acid in a dilute and impure state was certainly familiar to the sages and priests of ancient Egypt, and it may have enabled the mediæval alchemists to concoct cyanide solutions capable of dissolving gold. In modern times the cyanide process was first tried on a commercial scale in 1867 in the United States, but was apparently unsuccessful. The first real success, according to our author, was obtained by the McArthur-Forest Company in South Africa. It is estimated by experts that the gold deposit of the Witwatersrand is capable of yielding gold to the value of £215,000,000, of which one-third would not be won without this process.

The treatment is thus summarised: The process is most applicable to tailings, where the ores have already undergone plate amalgamation. The first stage is treatment with an alkaline solution, containing 4 ozs. caustic soda per ton of solution. By this means acids are neutralised, and organic matter is destroyed. Next follows the strong cyanide solution, from 0·3 to 0·5 per cent. of KCy, the quantity run on being one-third the weight of the tailings in the vats. This strong solution is allowed to act for three hours, followed by a gradual drainage for four hours. A weak solution, containing 0·15 per cent. of cyanide, is then run on to wash out the dissolved gold. Lastly comes washing with water to the extent of not less than 7 per cent. The dissolved metal is next deposited upon zinc shavings. The precipitation is influenced by a variety of conditions which have been carefully studied by Mr. W. Bottel, and are here quoted. The same authority has also studied the action of impurities and base metals in ores, which may prevent the solution of the gold and decompose the cyanide. Compounds of copper are very detrimental. The writer here suggests that weaker ores might in certain cases be treated with very weak solutions of cyanide with the co-operation of an electric current.

Such is the Siemens-Halske process. Here the gold is deposited upon thin sheets of lead. Weak solutions of cyanide, containing about ½ per cent, seem to have a selective action. The gold is dissolved, apparently not as potassium aurocyanide, but as simple auric cyanide. The electric current required is also feeble—a density per square foot of about 0·06 ampère. This process the author considers may prove a serious rival to the McArthur-Forrest process.

The work is written in a thoroughly practical spirit, and will prove invaluable to all interested in gold mining, whether metallurgists or as investors. The eleven plates, mostly drawn to scale, aid greatly in an understanding of the details.

Treatise relative to the Testing of Water-Wheels and Machinery, also of Inventions, Studies, and Experiments, with Suggestions from a Life's Experience. By James Emerson, Mass., U.S.A. Sixth Edition. 1894. 567 pp.

The author of this book, who is evidently on the best terms with himself, is very far from confining himself to water-wheels and turbines, which he understands. He wanders off into the fields of theology, politics, law, mythology, and ethics, subjects quite outside our competence. But he also seeks to belittle science and scientific men, from Newton downwards. He ascribes the telescope, the microscope, &c., to the mechanic! His motto is "The Mechanic to the Front"!—an aspiration for which in these days of strikes there is scant room. He lays down instructions for reaching the North Pole. On this subject one of his reviewers drily observes: "If the world gets in these latest pages of his literary work the best he is capable of rendering it, he cannot do better than set out for that undiscovered country and try his theory as he progresses."

CORRESPONDENCE.

NEW REAGENT FOR SHOWING THE PRESENCE OF HYDROGEN PEROXIDE IN GREEN PLANTS.

To the Editor of the Chemical News.

Sir,—I wish to direct your attention to the paragraph in Chem. News, vol. lxxi., p. 38, referring to A. Bach's "New Reagent for showing the presence of Hydrogen Peroxide in Green Plants."

In its essential features, *i.e.*, the use of aniline as a test, it is not new. I had the pleasure of assisting Dr. Schunck, F.R.S., a few years ago, in an investigation "On the Action of Aniline on Green Leaves and other Parts of Plants." As a result of this action, a definite crystalline substance was obtained, the properties and composition of which were determined. Our observations led us to believe that the brown colouration of the leaves under treatment, and the formation of the crystalline substance, were due to the presence in the leaves of hydrogen peroxide or an active oxidising agent of some kind. The results of the investigation were published in the *Annals of Botany*, vol. vi., July, 1893.—I am, &c.,

Geo. Brebner.

The Jodrell Laboratory, Royal Gardens,
Kew, February 13, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 5, February 4, 1895.

Argon.—M. Berthelot.—This memoir is in substance a reproduction of the communication made to the Royal Society by Lord Rayleigh and Professor Ramsay and already inserted in the Chemical News.

Monoiodoammonidic Derivatives of Hexamethyltriamidotriphenylmethane.—A. Rosenstiehl.—This investigation shows that methyl iodide forms with the complex triamines $A_3\equiv C-\overset{+}{R}$ two series of colourless compounds. The first series contains a single atom of nitrogen entirely saturated. The compounds of this class exchange the radicle $\overset{+}{R}$ with an acid radicle, and are transformed into colouring matters. The second series, formed by the addition of 3 mols. of methyl iodide, contains the atoms of nitrogen entirely saturated. The group $\overset{+}{R}$ in this case is not exchanged for an acid radicle, and does not become coloured.

Laccase, and on the Oxidising Power of this Diastase.—G. Bertrand.—The existence of an oxidising diastase is perfectly extablished by the author's experiments. The intervention of micro-organisms is excluded by the conditions of the process.

Reactions of Chelinodine with Phenols in Sulphuric Solution.—M. Battandier.—At the bottom of a porcelain capsule we place a drop of guaicol and about ½ c.c. of sulphuric acid of sp. gr. 1·84 and mix. At the edges of the capsule we then place some fragments of chelidonine, and cause the acid mixture to touch them, so as to moisten but not carry them away. The capsule being set on a table, we see in a few moments carmine streaks of a remarkable purity and intensity, descending from the fragments of chelidonine towards the bottom of the capsule. This reaction persists for a long time. When it succeeds well, it is one of the most beautiful possible, but it is rather capricious. I have not had the opportunity of trying the pure synthetic guiacol, but with the guaiacol carbonate it is much less intense. This manner of obtaining coloured reactions, which leaves free access for the oxygen of the air, is perhaps susceptible of generalisation. It has already yielded me good results with glaucine. Under the same conditions as guaiacol, thymol gives a rose colouration which lasts for more than twenty-four hours, only becoming slightly purple as the acid becomes hydrated. This reaction always succeeds if the chelidonine is introduced before the sulphuric acid gives a blue colour with the thymol. With ordinary phenol there is only a slight rose tint. Oil of cloves gives a purple, very distinct in spite of the yellowish brown colour which sulphuric acid produces with this oil.

Naphthol α gives streaks of dark green. Naphthol β gives streaks of a brown passing into a violet. Pyrocatechine, roses passing into a violet. Hydroquinone, yellowish streaks. Resorcine also gives yellowish streaks, but soon hidden by the blue colour which this phenol gives with the acid. Phloroglucine gives yellowish streaks passing to a buff. Pyrogallol produces reds, turning to a yellow and slowly disappearing. Gallo-tannic acid gives yellow streaks gradually passing into an intense grass-green. The ethers of the phenols act like the phenols themselves. It is known that chelidonine in a sulphuric solution turns green on the addition of a trace of nitric acid. All oxidising agents produce the same effect. The reaction is especially brilliant with a trace of potassium chlorate in solution or with an arseniate.

Zeitschrift fur Analytische Chemie.
Vol. xxxiii., Part 2.

Detection of Hydrogen Peroxide in Atmospheric Air and in Atmospheric Waters.—Em. Schöne.—The substance of this important memoir, which extends to nearly 50 pages, has been already inserted.

Volumetric Method for the Determination of Phosphoric Acid.—A. F. Holleman.—In the *Recueil des Travaux Chimiques des Pays Bas* (xii., p. 1) the author has communicated a volumetric method for the determination of phosphoric acid which reduces this determination to the titration of silver by the method of Volhard. The principle of the method consists herein, that in the solution of a phosphate, M_2HPO_4, the phosphoric acid is precipitated quantitatively as Ag_3PO_4, if care is taken to remove the nitric acid liberated by the addition of sodium acetate. If, therefore, we use an accurately known excess of a silver solution of known strength, after filtering off the Ag_3PO_4, we may determine (on Volhard's principle) the silver in an aliquot part of the filtrate, and hence deduce the quantity of phosphoric acid. The precipitation and filtration of the silver phosphate must be effected in a dark measuring flask, and a dark funnel, on account of the sensitiveness of this compound to light. If we have to determine the phosphoric acid in the acid solution of a phosphate, or in a solution of a primary phosphate (MH_2PO_4), it is necessary to add to the solution so much of an alkali that phenolphthalein just shows a change of colour. We have then again in solution the salt M_2HPO_4. For the details of this method I may refer to the memoir above cited. Dr. J. J. L. von Ryn has now re-examined this method in my laboratory on a series of solutions of $Ca_3(PO_4)_2$ in nitric acid, containing in 50 c.c. 94·9 up to 190·0 m.grms. P_2O_5, and obtained results given in a subjoined table. The values found agree well with those calculated, only when a large excess of the silver solution was used the phosphoric acid was found rather too high.

On Lard.—Dr. Samuelson.—All the qualitative reactions hitherto recommended for deciding on the purity of lard are not trustworthy, as, in spite of a negative result, a sophistication with a vegetable oil may exist. The iodine number is the main criterion.

Use of Micro-Chemical Reagents in Analytical Chemistry.—W. Lenz.—The "first communication" treats of the determination of ethereal oils, especially in cloves and mace. If possible, the author's methods will be reproduced *in extenso*.

New Execution of the Method of Schlösing for the Determination of Nitric Acid.—Prof. Dr. L. L. de Koninck.—This memoir requires the three accompanying illustrations.

Small Laboratory Apparatus.—Arnold Eiloart.—In this paper we have descriptions and figures of a suspended burette and of a syphon for maintaining a constant level of liquid.

Report on the Progress of Analytical Chemistry.—E. Hintz, with the co-operation of H. Weber.

MEETINGS FOR THE WEEK.

Monday, 25th.—Society of Arts, 4. (Cantor Lectures). "Means for Verifying Ancient Embroideries and Laces," by Alan S. Cole.
— Medical, 8.30.
Tuesday, 26th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Photographic, 8.
— Society of Arts, 8. "Mediæval Embroidery," by Miss May Morris.
Wednesday, 27th.—Society of Arts, 8. "Furnaces for Roasting Gold-bearing Ores," by C. G. Warnford Lock.
— British Astronomical Association, 5.
Thursday, 28th.—Royal, 4 30.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Meteorites," by L. Fletcher, M.A., F.R.S.
Friday, March 1st.—Royal Institution, 9. "The Children's Books of a Hundred Years Ago," by Rev. Canon Ainger, M.A., LL.D.
— Quekett Club, 8.
— Geologists' Association, 8.
Saturday, 2nd.—Royal Institution, 3. "Waves and Vibrations," by Lord Rayleigh, F.R.S.

THE CHEMICAL NEWS.
Vol. LXXI., No. 1840.

HALOGEN ESTIMATION IN ORGANIC COMPOUNDS.

By JAMES WALKER, D.Sc., Ph.D.,
Professor of Chemistry in University College, Dundee,
and JAMES HENDERSON, B.Sc.

Having had recently to perform a considerable number of estimations of the halogen elements in organic compounds by the method of Carius, we investigated the possibility of shortening and simplifying the usual operations by the adoption of a volumetric process. Our experiments have shown that the Carius method can be satisfactorily combined with the Volhard method for estimating silver, whereby a great saving of time and trouble is effected.

A weighed quantity of the substance to be analysed (usually 0·2 to 0·3 grm.) is heated in the ordinary way in a sealed tube with 2 or 3 c.c. of fuming nitric acid and a quantity of solid silver nitrate somewhat in excess of the amount necessary to convert the halogen into corresponding silver salt. The silver nitrate, however, instead of being roughly estimated in the usual way, is weighed off accurately and introduced into the tube preferably in the form of a single crystal. After the oxidation is completed, the tube is opened and the contents washed into a flask with four successive portions of water, the total amount of liquid being 100—150 c.c. The solution, with any precipitate that may have accompanied it, is boiled for ten minutes to expel the lower oxides of nitrogen. It is then cooled, and after the addition of iron alum as indicator, titrated with 0·05-normal solution of ammonium thiocyanate. The amount of thiocyanate required gives the quantity of silver nitrate still in solution, and this, when subtracted from the quantity originally added, gives the amount which has gone to form silver haloide with the halogen present in the organic substance.

In the following example the amount of bromine was estimated both gravimetrically and volumetrically with the same portion, the silver bromide obtained being filtered off and weighed, and the excess of silver nitrate titrated in the filtrate.

0·3458 grm. of substance was heated with nitric acid and 0·4044 grm. of silver nitrate. The amount of silver bromide obtained was 0·3664 grm., and the filtrate required 4·15 c.c. of ammonium thiocyanate solution (1 c.c. = 0·01724 grm. $AgNO_3$) for complete precipitation of the silver.

Percentage of bromine estimated gravimetrically	= 45·1
Percentage of bromine estimated volumetrically	= 45·3

A substance which was found by gravimetrical analysis to contain 33·85 per cent of chlorine gave the following volumetrical results:—

I. 0·3277 grm. substance required 20·0 c.c. of a thiocyanate solution (1 c.c. = 0·00812 grm. $AgNO_3$) after heating with 0·6930 grm. $AgNO_3$, whence Cl = 33·85 per cent.

II. 0·3114 grm. required 14·4 c.c. of the same solution after heating with 0·6183 grm. $AgNO_3$, whence Cl = 33·62 per cent.

These results show that the process is sufficiently accurate for ordinary purposes of organic analysis.

The method avoids filtration after the tube is opened, as only the *liquid* contents have to be washed into the receiving flask, it being a matter of indifference whether any of the precipitate remains behind or not. Again, it often occurs on opening a tube that small splinters of glass mix with the precipitate, which necessitates a tedious separation and weighing if the gravimetric method is adopted, whilst the volumetric method is thereby unaffected. If the thiocyanate solution, which should be standardised against a weighed portion of the silver nitrate used in the precipitations, is once prepared, the whole process may be completed in fifteen to twenty minutes after the opening of the tube.

PREPARATION AND PROPERTIES OF TITANIUM.

By HENRI MOISSAN.

Hitherto titanium has been more known in combination than in the free state. It has been previously obtained by Berzelius, Wœhler, Deville, and Kern only in the state of amorphous powders, the appearance and the properties of which varied with each preparation. The strong affinity of titanium for nitrogen, and the difficulty of obtaining a current of hydrogen absolutely free from nitrogen, have greatly complicated the production.

On heating in the electric furnace (100 ampères and 50 volts, 8 horse-power) titanic acid in a crucible, we regularly obtained a titanium oxide, fused or crystalline, of an indigo-blue colour. With a current of 300 to 350 ampères and 70 volts (40 horse-power) we obtain a bronze-yellow mass perfectly fused. This is the titanium nitride of Friedel and Guérin, Ti_2N_2. If we heat in the air in a boat of carbon under the action of an arc of 1200 ampères and 70 volts, the melted mass obtained is titanium carbide, TiC, absolutely free from nitrogen.

For obtaining titanium the author used the rutile of Limoges, carefully selected and containing very little silica and iron, but afterwards substituted titanic acid prepared in the laboratory. It is intimately mixed with carbon, compressed and dried. This mixture was strongly compressed into a crucible of coke of 8 c.m. in diameter, and placed in the middle of an electric furnace. We operated thus upon a quantity of 300 to 400 grms. The arc from a current of 1000 ampères and 60 volts was allowed to play for ten to twelve minutes. The crucible when cold was found to contain a homogeneous mass which had been melted only to a depth of a few c.m. Even with a current of 2200 ampères and 60 volts the fusion was not complete. Beneath the melted titanium was found a layer of yellow nitride, and at the bottom of the crucible a layer of blue titanium oxide. The best specimen obtained (carbide + oxide) yielded 48 per cent carbon and 2·1 per cent of ash. This fused mass may be mixed with titanic acid and, anew, submitted to the action of a current as intense as the former. By this method we obtained a titanium free from nitrogen and silicon, and containing only 2 per cent of carbon.

This titanium forms a mass with fractures of a brilliant white, hard enough to scratch easily steel and rock crystal. Its specific gravity is 4·87.

Chlorine attacks titanium at 325° with incandescence, yielding liquid titanium chloride, $TiCl_4$. Bromine produces at 360° a dark bromide. Iodine reacts at a higher temperature with visible incandescence, forming solid titanium iodide.

Titanium burns in oxygen at 610° with incandescence, leaving a residue of amorphous titanic acid. Sulphur attacks titanium slowly at the softening-point of glass. The sulphide is not attacked in the cold by hydrochloric acid, but with concentrated and boiling acid it gives off hydrogen sulphide.

In a current of nitrogen the powder of titanium forms nitride at a temperature bordering upon 800°. The combination ensues with a liberation of heat. This is the first distinct instance of the combustion of an elementary body in nitrogen. Carbon dissolves in melted titanium, forming a definite carbide. The excess of carbon crystallises out as graphite.

In the electric furnace silicon and boron combine with titanium, forming borides or silicides, melted or crystallised, and having a hardness equal to that of the diamond.

Titanium dissolves easily in melted iron and lead. With copper, tin, and chromium it yields alloys, which are under examination.

Hydrochloric acid, boiling and concentrated, attacks titanium slowly with evolution of hydrogen, producing a violet solution. With hot nitric acid the action is slow, yielding titanic acid. Aqua regia acts more rapidly. Dilute sulphuric acid dissolves titanium much more easily. Hydrogen escapes, and the solution has a violet colour. Titanium is attacked by melting potassium nitrate without apparent liberation of heat; but if titanium in powder is thrown into potassium chlorate heated to its decomposition-point, there ensues a lively incandescence. It is also attacked with incandescence by melting alkaline carbonates, and by a mixture of potassium nitrate and carbonate.

Powdered titanium heated in a current of steam does not decompose the vapour below a temperature near 700°, and the action is not continuous below 800°.

For the analysis of this compound it is melted with a mixture of two parts potassium carbonate and eight parts potassium nitrate. The white mass obtained is taken up in cold water; the insoluble residue is dissolved in cold hydrochloric acid and added to the first solution. The titanic acid is precipitated with ammonia.

The metal yielded:—Titanic acid 96·69, carbon 1·91, ash 0·41.

Titanium nitride forms very hard masses of a bronze colour; it scratches the ruby and cuts the diamond. Its specific gravity is 5·18.

Melted titanium is the most refractory substance which we have as yet obtained with the electric furnace. It is more infusible than vanadium, and goes far beyond pure chromium, tungsten, molybdenum, and zirconium. Melted titanium has a less affinity for nitrogen than the powders obtained by the action of the alkaline metals upon the fluotitanates. Still, this titanium, if reduced to powder, burns in nitrogen at a temperature of 800°.

In the totality of its properties, titanium distinctly approaches the non-metals, especially silicon.—*Comptes Rendus*, cxx., p. 290.

ON CERTAIN PERCEPTIBLE REACTIONS OF THE AMIDO-BENZOIC ACIDS.

By OECHSNER DE CONINCK.

These reactions have been employed by the author in analysing mixtures of amido- and nitro-benzoic acids.

He makes known the behaviour of the alkaline hypochlorites, hypobromites, and hypoiodites, of calcium hypochlorite, and of ferric chloride, in very dilute aqueous solutions.

I. *Action of Alkaline Sodium Hypochlorite on the Amido and Nitro-Benzoic Acids.*

With the ortho-amido acid the liquid turns to a blood-red. With the meta-acid, a red-brown. With the para-acid, an orange-red.

The three nitro-acids give no result under the same conditions.

II. *Action of Alkaline Sodium Hypobromite on the same Acids.*

With the ortho-amido acid the liquid takes a deep orange-red. With the meta- and para-acids, a bright orange-red.

The three nitro-benzoic acids give no result.

III. *Action of an Alkaline Sodium Hypoiodite.*

The author prepares the reagent by dissolving, in an excess of pure concentrated soda-lye, a little iodine until a yellow colour begins to appear.

With ortho-amido benzoic acid the liquid turns to an orange-red. With the meta-acid, a dull yellow. With the para-acid, a decided yellow. With the nitro-acids, nothing similar; the crystals of the ortho-isomer become deep yellow in contact with the reagent, but the liquids are not coloured as in the other reactions.

IV. *Action of Alkaline Potassium Hypochlorite.*

With the ortho-amido acid, a very deep red-brown. With the meta-acid, a dark red-brown. With the para-acid, a dark orange-red.

No coloured reaction with the nitro-benzoic acids.

V. *Action of Alkaline Potassium Hypobromite.*

With the ortho-amido benzoic acid the liquid takes a bright orange-red. With the meta- and para-acid, the same tint.

No result with the nitro-benzoic acids.

VI. *Action of the Alkaline Potassium Hypoiodite.*

This reagent has been prepared like the sodium hypoiodite. With the ortho-acid, a red-brown liquid. With the meta-acid, a deep orange. With the para-acid, a bright orange. With the nitro-benzoic acid, no colour.

VII. *Action of Alkaline Calcium Hypochlorate.* (*Dilute Solution.*)

With the ortho-acid, a deep violet colour, soon turning to black or to dirty green. This reaction is very sensitive. With the meta- and para-acids, a yellow-brown.

No reaction with the nitric acids.

VIII. *Action of Ferric Chloride in a very Dilute Watery Solution.*

With the ortho-acid, a rose-colour, turning to a wine-red. With the meta-acid, amber-yellow. With the para-acid, a red-brown.

No reaction with the benzoic acids, though the crystals of the ortho-isomer after a time take a light red colour.—*Comptes Rendus*, cxx., p. 100.

THE SEPARATION OF ARSENIC, TIN, OR ANTIMONY, FROM LEAD, COPPER, SILVER, CADMIUM, COBALT, NICKEL, &c.

(A Preliminary Communication).

By P. JANNASCH.

Some time ago I made known, in the *Zeitschrift fur Anorgan. Chemie*, a method for the quantitative determination of arsenic in sulphides (after previous oxidation) by a final heating in a current of dry hydrochloric acid vapour, and I described the apparatus in full.

For some time, in concert with F. Schmitt, I have been engaged with extending the dry hydrochloric acid process in general to the separation of arsenic from a series of other metals, and with the very best results. We used for our quantitative separations of arsenic an air-bath of nickel, capable of being closed and fitted with thermometers and windows of mica, in which my glass apparatus (formerly described) can be heated to given temperatures up to 450°. The metals to be separated, or their compounds, are dissolved in the glass apparatus with nitric acid or aqua regia, &c., dried therein, and then distilled at the required temperature in a current of hydrochloric acid gas. The arsenic, collected in especial receivers, is then separated and weighed. In a separation of arsenic and tin, attempted in this manner, we observed the great solubility of the tin chloride present, and have thereupon set about the direct separations of this metal from less volatile metals, such as lead, copper, &c. Here the tin also is collected in especial receivers, subsequently precipitated from the solutions as tin sulphide by means of ammonia, and ammonium sulphide with acidulation, and finely weighed as tin oxide.

The statement of Drown and Eldridge (last issue of the *Zeit. Anal. Chemie*) on the volatility of tin chloride has induced me to make this preliminary communication in order to secure the continuation of our work on the lines we have hitherto taken for the direct separation of tin from the less volatile metallic chlorides. Drown and Eldridge have already effected the indirect separation of lead and tin by the repeated evaporation of their chlorides, and we have already obtained the same separation in a direct manner by volatilising the tin in a dry current of hydrochloric acid at 200°, collecting the distillate of stannic chloride in receivers containing water acidified with hydrochloric acid. We reserve full accounts of our separations of arsenic, tin, and antimony, from the less volatile metals, and analogous experiments in a current of dry hydrobromic acid gas.

EXCLUSION OF SULPHURETTED HYDROGEN IN QUALITATIVE ANALYSIS: ITS REPLACEMENT BY THIOACETIC ACID.

By ROB. SCHIFF and N. TARUGI.

If to a hydrochloric solution of the metals of the second group we add a faintly ammoniacal solution of ammonium thioacetate, and heat to near the boiling-point, the metals are at once deposited as sulphides, and the odour of sulphuretted hydrogen given off is very slight. After cooling and filtration there is found in the filtrate no trace of metals, even if arseniates were originally present, the complete precipitation of which by present methods is well known as exceedingly difficult.

The mixed sulphides are separated by the ordinary methods, and the filtrate—after being boiled for a few minutes—is used for the recognition of the next following groups. From ½ to 1 grm. of material are taken for analysis, and for such quantities 1·5 to 2 c.c. of a 30 per cent solution of ammonium thioacetate is in general sufficient for a thorough precipitation. Sulphur is never deposited during the reaction, and no disturbing products are introduced in the operation. The reagent—

$$CH_3.C : O(S.NH_4)$$

is easily obtained by the action of glacial acetic acid upon phosphorus pentasulphide; it boils at 95°, has an unpleasant odour, and is sparingly soluble in water. If the acid is dissolved in a slight excess of dilute ammonia, we obtain a yellowish liquid of a faint odour, resembling that of ammonium sulphide. It is diluted to three times the volume of the original acid. It is served out to the students in small bottles, through the cork of each of which is thrust a pipette holding about 2 c.c.

Arsenites and arseniates give in the cold a whitish turbidity, but in heat an immediate and complete precipitation of arsenic trisulphide.

Bismuth, copper, and stannic and stannous salts are partially precipitated in the cold, but completely in heat.

Lead salts, in the cold, a dark red precipitate, which if heated changes to lead sulphide.

Silver salts.—Silver chloride, dissolved in hot concentrated hydrochloric acid, is completely precipitated as silver sulphide. Silver chloride, bromide, and iodide, if heated with a solution of thioacetate, are completely converted into silver sulphide.

Cadmium salts.—The sulphide is known to be moderately soluble in hot hydrochloric acid. Whilst being heated with the reagent in a hydrochloric solution the precipitate sometimes dissolves, but it is re-deposited when cold.

Mercuric salts.—In the cold a red precipitate (sulphochloride); in heat, conversion into black sulphide.

Platinum salts.—Cold, a red precipitate; in heat, a complete conversion into platinum sulphide.

Gold salts.—Exactly like platinum.

Ferric salts.—Instantly reduced to ferrous salts.

Chromic salts.—Instantly reduced to chrome salts.

Aluminium, manganese, nickel, cobalt, zinc, &c.—Salts in acid solution are not affected.

The nickel, cobalt, and zinc, &c., sulphides in ammoniacal solutions, are at once thrown down. But we see no reason for substituting ammonium thioacetate in separating metals of the fourth group.—*Berichte*, vol. xxvii., p. 3437.

CRUCIBLE TOOL-STEEL.

By SERGIUS KERN, M.E., St. Petersburg.

In the summer of last year, we constructed at the New Admiralty, St. Petersburg, a coke furnace for melting crucible steel. Into the furnace four crucibles are placed, which contain each a charge of 80 pounds. The daily output is eight poods of crucible tool-steel, or soft steel for castings, as besides preparing tool-steel ingots (4 inches × 4 inches) we introduced the manufacture of steel castings, weighing up to 5—6 poods (1 pood =36·11 English pounds).

This Government establishment, the New Admiralty, has three ship-building yards; out of them, two are substantial brick structures, and the third is wooden. The climate here commands closed yards. For the working of mild sreel in the construction of war-ships, nearly exclusively foreign tool-steel was used. The necessary steel castings, if wanted, were ordered at the steel-works situated in St. Petersburg.

We constructed the steel-melting furnace in the iron-foundry of the Admiralty, using the existing chimney for the boiler and copper-melting furnaces. Want of space and other reasons induced us to alter the ordinary adopted dimensions. The soft iron for the melting and the crucibles were supplied by the Obouchoff Steel Works. The works prepare this iron from the steel turnings of their mechanical shops, where ordnance is manufactured; the iron is very clean.

Carbon	0·12 per cent
Manganese	0·07 ,,
Silicon	0·11 ,,
Sulphur	0·01 ,,
Phosphorus	0·02 ,,

For the manufacture of tool-steel we melt this iron with a certain amount of refined Swedish pig-iron. When melting for steel castings, the charge consists of iron mixed with puddled steel or scrap in the form of rounds, received during the punching of holes in ship plates. The latter is a cheap and good substitute for puddled steel. The steel castings have the following composition:—

Carbon	0·47 per cent
Manganese	0·33 ,,
Silicon	0·14 ,,

The castings are all annealed, and in this case we find that steel of this chemical composition is specially suitable.

We use ferro-aluminium for small castings, but for castings of more than 3 poods prefer silico-spiegel (10 per cent of silicon, 14 per cent of manganese). In heavy castings, weighing several tons, the use of ferro-aluminium is nothing more than waste of money.

The tool-steel ingots, weighing two poods each, are hammered into sizes in the forge of the Admiralty. If thus the tool steel is manufactured on a small scale by the shipyard itself, we must conclude that this operation will be always a remunerable business, especially when at intervals of this line of work small steel castings are made which are often wanted in ship-building.

THE ABEL TEST.

By J. H. B. JENKINS.

In the accompanying diagrams the rate of heating of a burning petroleum oil in the Abel flash-point apparatus is shown. In Fig. 1, the usual conditions are represented; the temperature of the water-jacket falling from 130° F., whilst the oil's temperature is raised from 60° F. In Fig. 2, the initial temperature of the water-jacket is 180° F., whilst the oil starts on one occasion from 60° F., and on another from 90° F.

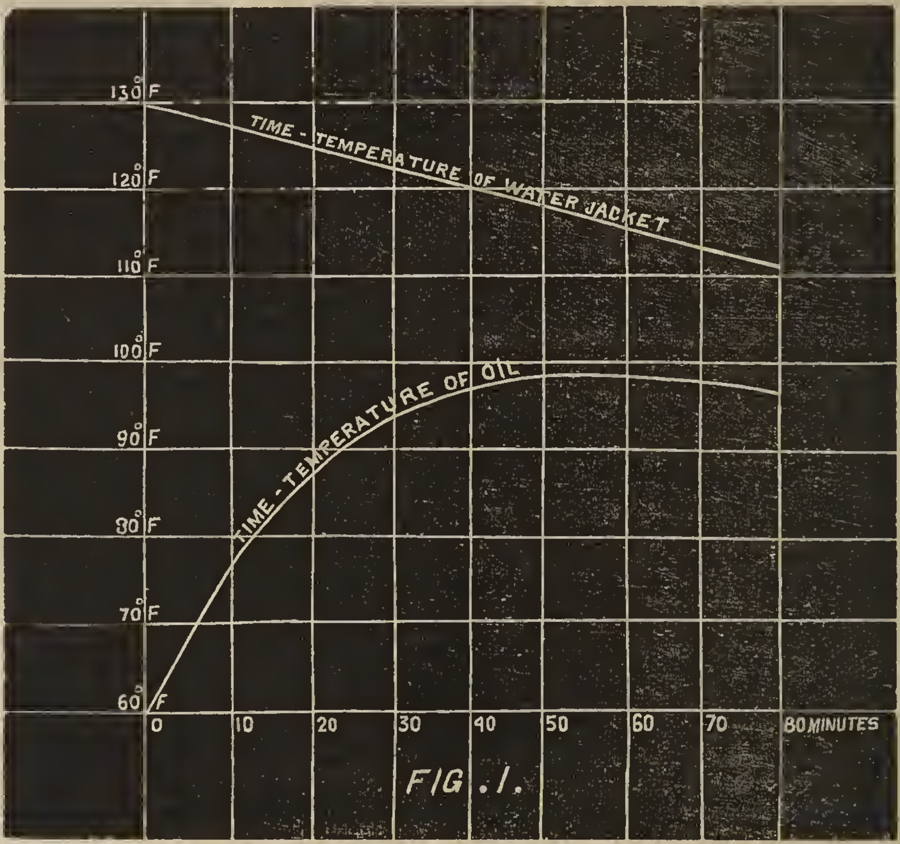

FIG. 1.

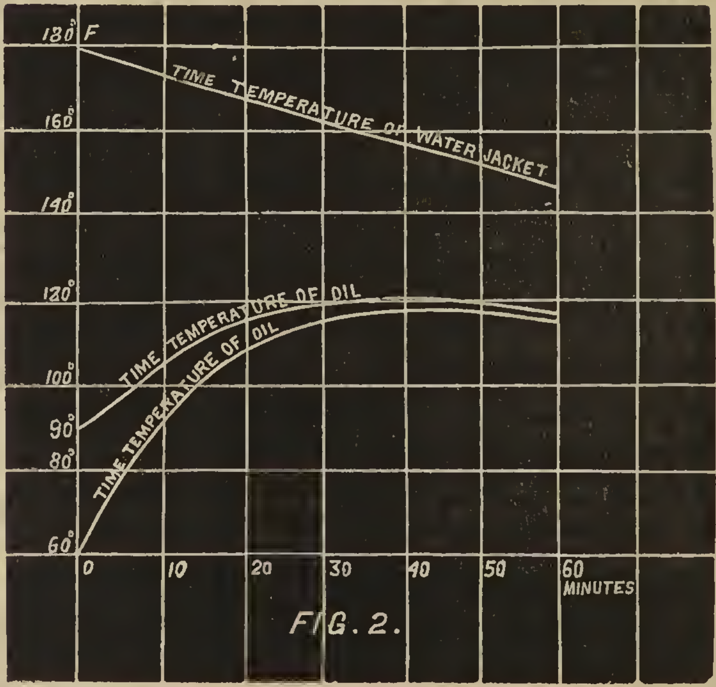

FIG. 2.

From Fig. 1 we see that just after the start the rate of heating of the oil approximates to 3 degrees per minute. Twenty minutes later, the rate of heating is only one-fourth as great, and the temperature of the oil is about 90° F. An hour after the start, the oil reaches its maximum of about 99° F., and after remaining for many minutes, it slowly falls again.

A consideration of the design of the instrument shows that many likely sources of error in flash-point determinations are obviated by it, though its applicability has been consequently narrowed. The apparatus, used without modification, is only applicable to oils flashing below, say, 90° F., and even up to that temperature the rate of heating is about four times as great at first as it is at last, What is wanted is an apparatus in which the oil would be heated regularly, and which would serve, without modification, to test all burning oils up to 130° F. or 150° F. flash-point.

It might be well if some such body as the Society of Public Analysts or the Society of Chemical Industry were to express an opinion as to the highest flash-point which should be taken by the Abel apparatus used without modification, and then exactly in what way the conditions of testing should be altered. This would lead to more uniform results for high flash-points.

Are the instruments standardised by the Board of Trade with a pendulum 24 inches long or only 13 inches long, such as they are issued with? Is there no way of preventing the pendulum mistake being repeated?

The suggestion has been made of a stirring arrangement to mix up the oil vapour and air in the cup, but the advantage would scarcely compensate for the extra complication of the apparatus, and may prove a fresh source of error. It cannot be insisted that the Abel test will detect quite the lowest temperature at which the vapour of an oil may be flashed under any possible conditions; but if oils of identical inflammability give the same flash-point by the apparatus, and the flash-point given is always proportional to the inflammability, it is better to retain the present simplicity of the instrument, rather than aim to get results a degree or two lower by less certain methods.

Sometimes the flash-point of an oil obtained from different instruments may be reported as varying a few degrees; this may be partly dependent upon an earlier partial flash, which sometimes escapes notice, but which leaves in the vapour-space sufficient combustion products to delay the next flash for two or three degrees.

G.E.R. Laboratory, Stratford, E.,
February 13, 1895.

THE SECRET OF THE BROWNIAN MOVEMENTS.*

By R. MEADE BACHE.

(Concluded from p. 97).

Fixed oils have not the same molecular constitution as volatile oils, nor these the same as alcohol, nor either the same as water. Whatever these differences may signify in various behaviours under varying conditions, one, among the rest, distinguishes water from the rest and all other liquids. Despite its apparent perfect fluidity, the reluctance of its molecules to move among themselves as smoothly as do those of other liquids among themselves is one of its most evident characteristics. We see this exemplified by the way, long since ably demonstrated, in which a wave is built up from ripples, by the way in which the surf breaks along the shore, and in the ease with which a small proportion of oil in contact with water modifies or subdues its energy. Only recently I steered a boat in Boston harbour between two headlands, between which, and far beyond, white-caps covered the surface of the water, surrounding a placid lakelet of a square mile in area, black by contrast to its white-capped margin, over the surface of which lakelet I was soon smoothly gliding; and this change from turbulent to placid waters was wholly due to the merest film of oil from Boston's great sewer discharging its contents three miles away on the lowering tide from the head-house on Moon Island into the current running towards the sea. I am aware, of course, that part of the calmness described was owing to the fact that the oil lessened the friction of the wind on the water. But that was not the only cause of the calming effect produced by the oil. Oil prevents the friction of parts on the surface of water already in agitation, and thereby quiets the wave already risen. The area which I have just described as a smooth lakelet had been only a short time before my arrival at the place in precisely the same state of agitation as the surrounding waters. The surface is the part where the wave begins to form, and where it receives constant increments, the wind propagating these, and by impact on the growing wave or billow as a whole, forming and propelling it as a mass, despite its tendency in deep water to oscillate freely in the vertical without translation horizontally. It is easily conceivable that, although particles of oil may, as I have stated, experience no sensible friction when in contact with the molecular movements of water, so almost infinitesimal are they in range, yet that oil forming a film over a large surface of water may, through friction, as an enclosing sheath, tend to quiet the water, and thus impair and gradually destroy its ability to continue the massed effect known as a wave, at the place, the surface, where not only is it generated, but where it most effectively tends to preserve its energy of movement.

Thus, it is not only through its weight that water, when set in active motion, becomes so formidable as we know it to be when in angry mood. It is because, besides the momentum with which it can be endowed through its great weight, it lends itself, through its molecular constitution, to the storage of enormous energy and to the yielding up of that energy reluctantly. Assuming the existence of a sea of oil or one of alcohol, and either in a state of turbulence, and moreover eliminating in imagination the difference in weight between these and water, either in comparison with water equally turbulent would gently come to rest.

The difference between Herr Wiener's view and mine is radical. He speaks of the motion common to fluids as the cause of the brownian movements. But such motion, at least as perceptible through the microscope, does not exist, except in water or in some other liquid in which water is, as I have proved by experiment, a considerable constituent. Then Herr Wiener, although accounting for the brownian movements by hypothetical movements common to all fluids, really makes their causation the vibratory effect of rays of light and heat, to which, he thinks, fluids through their constitution lend themselves. I, on the contrary, show that the molecular motion, called brownian, taking place under all conditions imposable, is a property of water and of water only, and that light and heat have naught to do with producing it, although, as I have admitted, they may possibly act in intensifying it. All that I may claim to have detected is a phenomenon which reverts to the molecular constitution of water, as to which the moving solid particles in it concerned in the brownian movement have no more to do than has a current-metre to do with the flow of the stream the swiftness of which it measures. We do not deny that a gas may be essentially pure, and therefore homogeneous, a chemical as well as physical entity, and that, nevertheless, its molecules may have repulsions among themselves: on the contrary, we affirm it. Similarly water, recognised, as it is, as a chemical condition, not a mechanical mixture, has, as here demonstrated, repulsions among its molecules.

When I take into account all that I have detailed, and remember also that these moving particles of which we have been speaking, hermetically sealed under glass, as I have them now under cover-glasses, move indefinitely in time, unmodified in range and velocity, through changes of temperature, through light and darkness, through electricity and magnetism, in the presence of every force to which I have been able to subject them, I cannot but think, when I add that these movements are active in proportion to the fineness of sub-division of the particles, that they are caused by the mutual repulsions of the molecules of aqueous fluids. Did I see a relatively large mass moving as vigorously as the most minute one visible

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* Read before the American Philosophical Society, April 20, 1894, —From the *Proceedings of the American Philosophical Society*. xxxiii., No. 145.

to the eye, I should regard this theory as untenable from that single fact alone, because it would be impossible that molecular action should concentrate effect on a relatively great mass; but when I see, as I do, the largest masses remaining unmoved, and descending in the scale, smaller ones, showing the effects of a faint impulse, and descending further still, others exhibiting sluggish movement, until the sight reaches the smallest particle visible, finding in that the most eccentric and vehement movement of any exhibited, I know then that I am looking at a sea where the little waves dash in vain on the impressionless rocks, barely disturb the floating ships and hulks, but twist and swirl and make frantically dance the little cockle-shells of boats wherever they may happen to be upon the surface; and that, in fine, I am witnessing the molecular movement of this sea in its effort to escape into space. The aqueous fluids, finding no release, as under my cover-glasses, the movements would go on for ever; finding it in freedom from confinement, they go on until the fluid which is the condition of their manifestation is in a few minutes dissipated in evaporation.

I must confess that, although every conclusion reached through labour bestowed gives a certain pleasure in legitimate appetite for knowledge gratified, yet this is so far beneath what I had thought might lie hidden under the mystery of the brownian movements, I experience a sense of disappointment. I had thought that this investigation might be one of the paths that lead to the solution of the question whether or not energy is immanent in matter or a thing apart from it. For many years after the beginning of this century nothing fundamental in physics was known beyond the fact that matter is indestructible. It has been learned since, but no longer ago than about fifty years, that energy also is indestructible. It still remains, perhaps, to be shown that energy is but an emanation and manifestation of matter reacting on it. Advanced as our knowledge is within a few years as to molecular movement, I had hoped that the investigation of the brownian movements might yield some contribution to molecular theory, and thence lead to a profounder knowledge than we now possess of molecular behaviour in the abstract. I am able, however, to claim for the demonstration here no more than that the brownian movements are not the self-movements of finely divided particles in suspension in aqueous solutions, which Herr Wiener had also ascertained, but simply that which he did not ascertain, movements generated by the molecular action of aqueous fluids, instead of being, as he and Herr Exner also thought, in differing form, phenomena due to light and heat. Perhaps even this moderate conclusion may be disputed, but it remains to be disproved.

Determination of Fat in Cheese.—Stefan Bondzynski.—The author's method consists in introducing a measured quantity of milk into a suitable tube, mixing the milk with concentrated hydrochloric acid, and heating until the precipitated casein is re-dissolved. Ether is then added, and the fat is determined in a known volume of the ethereal solution. This method is applicable to the determination of the fat in cheese. A portion of the cheese is ground up to a fine paste, and a weighed quantity is introduced into a tube, and mixed with 20 c.c. of hydrochloric acid of sp. gr. 1·1. On cautiously heating upon a wire netting, the cheese dissolves and the fat collects in a fused state on the surface. The tube is cooled, and about 30 c.c., of ether added. The fat dissolves quickly when the contents of the tube are allowed to stand at a temperature of about 40°, when the strata of acid and of ether-fat separate sharply from each other. The volume of the ether-fat solution is read off, 20 c.c. are drawn off with a pipette and introduced into a tared Erlenmeyer flask; the quantity is determined, and calculated for the entire ethereal solution.—*Zeit. f. Anal. Chemie.* xxxiii., Part 2.

A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF NITROUS OXIDE.

By GEO. T. KEMP.

(Preliminary Communication).

The necessity for further research on the methods for the quantitative determination of nitrous oxide is readily seen from a brief review of the past work on the subject. The method most frequently employed is that recommended by Bunsen,[*] which consists in exploding with hydrogen, by which the nitrous oxide is reduced to water and nitrogen according to the equation—

$$N_2O+H_2=N_2+H_2O.$$

The shrinkage in volume after the explosion is equal to the original volume of nitrous oxide present. This method has not met with general favour, as several observers have found the reaction not to be a clean one, side reactions giving rise to oxidation or reduction products, according to different conditions varying with the ratio of hydrogen to nitrous oxide and with pressure.

Frankland[†] refused to report positively on the question as to whether nitrous oxide was decomposed in the human body during anæsthesia, as he had no satisfactory method of determining the nitrous oxide in the inhaled and exhaled air. He says, "The separation of nitrogen and nitrous oxide presented quite unlooked-for obstacles, since their explosion with excess of hydrogen, instead of liberating free nitrogen from the nitrous oxide as commonly supposed, gives rise to the formation of nitrous acid and ammonia likewise." Using a large excess of hydrogen, and exploding under reduced pressure, gave better results, but "not so sharp as he could wish."[‡]

Practically the same side reactions have been encountered by Goltstein, Winkler, and Lunge. Goltstein[§] speaks of the method as "Höchst ungenau." Lunge[||] says that with hydrogen or oxyhydrogen side reactions, which render the results useless, readily take place.[¶] Winkler[**] hoped to avoid the side reactions mentioned above by passing the gases over palladium asbestos; but though the decomposition into nitrogen and water took place readily, the results were not constant. A white cloud of ammonium nitrate or nitrite was sometimes seen. The method has been advocated by Dummreicher and by Hempel. Dummreicher,[††] apparently, was not acquainted with the adverse criticisms on the method, for he says that Bunsen's work was the only one with which he was familiar. He found that the method gave satisfactory results, and spoke of the reaction as smooth (glatt).

Hempel[‡‡] also advocates explosion with hydrogen. Replying to Lunge's[||||] article, which called attention to side reactions, he makes no criticism beyond saying that these were likely due to impurities in the gas. The purest gas which Hempel obtained from ammonium nitrate was 98 per cent N_2O, and 2 per cent N. He exploded this gas with hydrogen, in varying proportions alone, and with the admixture of oxyhydrogen gas. He finds the best mixture of hydrogen and nitrous oxide to be when—

$$N_2O : H :: 1 : 2 \text{ or } 3.$$

When oxyhydrogen gas is added it should be in such proportion that, independent of the amount of nitrous oxide and hydrogen, there shall be 26 to 64 volumes of oxyhydrogen gas to every 100 volumes of non-explosive

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[*] Bunsen, "Gasometrische Methoden," 1878, p. 60.

[†] *Transactions of Odontological Society, Great Britain*, 1872-73.

[‡] *Op. cit*, p. 20.

[§] Goltstein, *Arch. f. d. gesammt. Physiologie*, 1878, p. 338.

[||] Lunge, *Berichte*, xiv., p. 2190.

[¶] "Bei der Verbrennung mit Wasserstoff oder Knallgas treten dann leicht unangenehme Nebenreactionem ein welche die Resultate unbrauchbar machen."

[**] Winkler, "Industrie Gaze," ii., 1877, p. 427.

[††] Dummreicher, *Monatsheft für Chemie*, 1881, i., p. 732.

[‡‡] Hempel, *Berichte*, 1882, xv., p. 903.

[||||] Lunge, *loc. cit.*

gas.[*] He exploded with hydrogen when the ratio of H to N_2O was as low as 1·6 : 1, in which experiment the explosion was so violent as to break the apparatus, but he does not mention any side reactions. When—

$$N_2O : H :: 1 : 4·6,$$

he found the mixture to be no longer explosive. He makes no mention of having tested his residual gas for ammonia after any of his explosions.

It may be of interest to add that Bunsen himself speaks of this, his method, as not being entirely satisfactory, but he does not speak of side reactions. In his "Gasometrische Methoden" he only gives one experiment, and, as far as I can find, this is all he made.

Several other methods for determining nitrous oxide have been suggested, but none are without objection; and a careful review of the literature has shown that only one of these methods has advocates besides the author who proposed it. This method is one proposed (for nitrous oxide) by Lunge,[†] and consists in absorbing the nitrous oxide by a considerable quantity of absolute alcohol, and allowing for the amount of other gases absorbed. Alcohol has a high coefficient of absorption for nitrous oxide in comparison to other gases. Lunge says the results by this method are always too high. For example, from a mixture containing 53·1 per cent of N_2O, he obtained 54·7 per cent. This method was used by Goltstein,[‡] who found it superior to exploding with hydrogen, and, on the whole, satisfactory.

After finding that ammonia was formed in the reaction of nitrous oxide with hydrogen in the presence of an excess of hydrogen over platinum or palladium asbestos, Winkler[§] suggests that a large excess of hydrogen be added, and that the gas be subjected for some time to the action of weakly heated platinum or palladium asbestos, claiming that the nitrogen of the nitrous oxide is, for the most part (der Hauptsache), transformed into ammonia. The ammonia is then determined by standard acid. He recommends this method in cases where the amount of nitrous oxide is very small.

Lunge[||] has tried this method, and criticises it severely. He finds that a comparatively small amount of the nitrous oxide is converted into ammonia. Another method suggested by Winkler[¶] is to pass nitrous oxide over a glowing palladium wire in a tube or in a grisoumeter. The nitrous oxide is split up according to the following reaction:—

$$\underset{\text{2 vols.}}{2N_2O} = \underset{\text{3 vols.}}{2N_2 + O_2},$$

so that the amount of nitrous oxide present is equal to twice the increase in volume. Winkler says of this method that it is the only one which has given really satisfactory results. Lunge has tried this, but says it is not quantitative. Moreover, the decomposition is not a clean one, as various oxides of nitrogen are formed and the mercury is attacked. The presence of nitrogen peroxide, NO_2, was shown by the gas becoming brown.

The author of the present paper was led into the investigation, of which it is an account, by being confronted, in some pharmacological work on anæsthesia by nitrous oxide, with the problem of determining nitrous oxide in the presence of nitrogen, the total amount of gas being only 4 or 5 c.c., and the nitrous oxide an unknown part of this, but likely as much as 80 or 90 per cent, thus leaving an exceedingly small residue of nitrogen.

Both Bunsen's method of exploding with hydrogen, and Winkler's method of decomposing the nitrous oxide over a hot palladium[**] wire were tried, but the results obtained were decidedly unsatisfactory. In working with nitrous oxide all the manipulation of the gas must be carried on over mercury, as water absorbs a considerable amount of the gas. In decomposing nitrous oxide with a glowing platinum wire, in a grisoumeter over mercury, the author's results were similar to those obtained by Lunge, viz., the gas became brown, showing the presence of nitrogen peroxide, NO_2, and though it might clear up, showing a possible decomposition of the NO_2 into nitrogen and oxygen, there was always a thick brown layer where the surface of the mercury had been attacked, thus binding the oxygen in a way which makes the method useless.

After a large number of determinations by exploding with hydrogen, I was forced to agree unequivocally with previous observers who found the method inaccurate because of side reactions. This could not be due to impurities in the nitrous oxide, for that was prepared by the method suggested by Dummreicher[*] of surrounding the retort, in which the ammonium nitrate is heated by a bath of molten metal of low fusing-point. By taking this precaution to obtain uniform heating of the fused ammonium nitrate, and selecting clean well-formed crystals, the fused mass remained clear as water and the decomposition was a clean one, yielding N_2O about 100 per cent pure, as shown by the analyses by the carbon monoxide method, which will be described later.

After exploding nitrous oxide with hydrogen in the Bunsen eudiometer in such proportions as to form an explosive mixture, and finding the results unsatisfactory, I was informed by Prof. Orndorff, of Cornell University, of some unpublished experiments of Mr. B. S. Cushman, in the Cornell laboratory, in which he found that mixture of gases no longer explosive (*e. g.*, oxygen and a large excess of hydrogen) could be smoothly burned out over a glowing platinum wire in a grisoumeter, the results being, if anything, more satisfactory than by explosion. Hoping that by avoiding the violent reaction of explosions, and using a larger amount of hydrogen, I might escape the side reactions, I made a series of combustions in the grisoumeter, and at first felt encouraged, for there was no evidence of the formation of the oxides of nitrogen or their acids in the presence of the large excess of hydrogen, and the mercury was not attacked.[†] The results were discordant, however, some coming out exactly, and some varying widely from 100 per cent and from each other. In all experiments but one the reading was exact, or there was too much contraction after combustion. This persisted after extra precautions were taken to prevent the possible escape of hydrogen. The only explanation that suggested itself was the formation of ammonia, which, so far as I know, has never been tested for in such experiments. The test was made, after combustion, by bubbling the gas through ammonia-free water, in a Varentrap bulb, and treating this water with Nessler's solution. The results varied from a negative test to a deep yellow colour, showing the formation of ammonia in varying amounts in the different experiments, which proves the method to be untrustworthy. Washing out the grisoumeter and testing the wash-water gives a better result than bubbling the residual gas through water and testing that. It seems that most of the ammonia is absorbed by the water formed in the reaction, which condenses on the surface of the mercury and on the glass. I was not able to find any factor that governed the formation of ammonia, unless it was true that the hotter the wire the greater was the tendency for its formation. Within the limit of the few seconds or minutes required for combustion, the time did not appear to have any effect. The addition of oxyhydrogen gas did not prevent the formation of ammonia. Two such experiments were made, in both of which ammonia was formed. The ratio of oxyhydrogen gas to the excess of hydrogen beyond that needed to unite with the oxygen of the nitrous oxide was as 8 to 100 in one case, and as 15 to 100 in the other. The explosions were quite violent, and I feared to add as

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[*] *Op. cit.*, p. 910.

[†] Lunge, *op. cit.*, p. 2191.

[‡] *Arch. f. d. gesammt. Physiologie*, 1878, p. 337.

[§] *Op. cit.*, p. 429.

[||] Lunge, *Berichte*, xiv., p. 2191.

[¶] Winkler, "Industrie Gaze," ii., 1877, p. 260 and p. 426.

[**] In the author's experiments only platinum wire was used.

[*] *Monatsheft f. Chemie*, 1880, i., pp. 735, 741, and 742.

[†] In a few experiments an exception is noted, but always as doubtful and trifling in amount.

much as Hempel recommended* (26·64 to 100), lest by breakage of the apparatus I should bring the work to a temporary standstill. These experiments differ from Hempel's, also, in being made in the grisoumeter over a glowing platinum spiral instead of with the spark, so that they are not in every respect comparable.

Since hydrogen gave such little promise of success, I tried various methods for reducing the nitrous oxide with carbon. The first method employed was to pass a series of electric sparks between specially constructed carbon electrodes. This decomposed the gas more rapidly than it reduced it. Carbon monoxide and carbon dioxide were formed, but oxides of nitrogen were formed at the same time. The mixture became brown and the mercury was attacked. The next method yielded better results. A piece of gas carbon was filed into a small cylinder about as thick as a match stick and about 6 m.m. long. A platinum spiral was coiled around this, and the whole introduced into the grisoumeter. Upon closing the circuit the spiral glowed and heated the carbon. In an atmosphere of nitrous oxide the carbon burned with great intensity, and reduced the nitrous oxide to CO and CO_2. Thinking that cyanogen might be formed in this reaction, as ammonia had been with hydrogen, I tested the residual gas in several experiments, but not a trace of cyanogen was found. I hoped by continuing the combustion to get all the gaseous carbon in the form of carbon monoxide, which would have doubled the volume of gas after combustion and halved the error of reading, thus—

$$\underset{\text{1 vol.}}{N_2O + C} = \underset{\text{2 vols.}}{N_2 + CO.}$$

This I found to be impossible, however, for even at the and of an hour's combustion there was a considerable amount of carbon dioxide present. To have determined the amount of nitrous oxide originally present, from the carbon monoxide and carbon dioxide formed in its reduction, would not have been as convenient as the next method tried, which proved to be both convenient and accurate. This method consisted in burning the nitrous oxide with a considerable excess of carbon monoxide in a grisoumeter, and determining the CO_2 formed, from which the nitrous oxide could be calculated. Before I had taken up the grisoumeter work on hydrogen, Prof. Morse suggested to try explosion with carbon monoxide. While working with Bunsen eudiometers I tried this, but found the results unsatisfactory. With a small excess of carbon monoxide the explosion was violent; with a large excess the mixture would not explode, and in no case was the nitrous oxide completely reduced. Somewhat better, though not satisfactory, results were obtained by explosion in the grisoumeter later. Whether the difference is due to the different pressures in the two forms of apparatus I am unable to say, but it appears the most likely explanation. My own results in the experiments on nitrous oxide and hydrogen in the grisoumeter were quite in accord with the more extended observations of Cushman, already referred to, as to the ease and completeness with which non-explosive mixtures may be burned out over a glowing platinum spiral; so I determined to apply this method to the mixture of nitrous oxide and carbon monoxide, which had not yielded satisfactory results on explosion.

The grisoumeter usually employed for combustions over water† is not suitable for use with mercury, so that a proper form was improvised by using an ordinary Hempel pipette for solid reagents. To fit into the neck of this is chosen a rubber stopper with one hole. Through this hole is passed a piece of glass tubing, open at each end, but drawn out so as to form a shallow neck about 10 m.m. from the end which extends into the grisoumeter. The lower end (below the stopper) is bent into a gentle curve, or an obtuse angle, for convenience of connection with a rubber tube. Into this glass tube, at any convenient point below the stopper, a piece of platinnm wire is fused. The platinum spiral is made of fine wire, which is twisted, at each end, on to a piece of heavier platinum wire, so thick as not to be much heated by a current which will glow the spiral. The piece of stout wire connected with one end of the spiral is passed into the open end of the glass tube; the piece at the other end of the spiral is twisted two or three times around the constriction in the tube, for firmness, and the end then allowed to hang down beside the tube. The wire should be of sufficient length to reach to at least 40 m.m. below the top of the tube, after having passed twice around the constricted neck. The spiral can now be fixed in any convenient position above the top of the tube by bending the stout wire. Connected with the lower end of the glass tube outside the grisoumeter is a piece of rubber tubing somewhat longer than the grisoumeter is high. To the free end of this is attached a funnel, by which the rubber and glass tube may be filled to the top with mercury. When so filled the rubber tube is closed, bp a stout pinchcock, close to its connection with the glass tube, The funnel is supported by a separate stand. The platinum wire fused into the glass tube below the cork is thus connected, with the spiral, by the column of mercury in the tube, and, when the mercury stands high enough in the grisoumeter to touch the platinum wire on the outside of the tube, the circuit can be closed through the spiral by connecting one pole of a battery with the platinum wire fused into the glass tube, while the other pole is connected with the mass of mercury filling the grisoumeter. This is best done by an iron wire passed straight down through the small bulb of the grisoumeter until it strikes the mercury.

The results of my experiments with this method are given in the following table. It must be borne in mind that the readings were all made in Hempel's burettes for technical gas analysis, and that these were not specially calibrated, so that the probable error is about ±0·1 c.c.

Experiment.	Taken c.c.	Found c.c.	Ratio. $CO : N_2O$.
August 28, Burette 3 ..	9·8	9·8±0·1	5·0 : 1
,, 28, ,, 2 ..	9·7	9·7 ,,	6·4 : 1
,, 29, ,, 1 ..	4·8	4·7+,,	13·8 : 1
,, 29, ,, 4 ..	3·3	3·5 ,,	21·0 : 1
,, 30, ,, 3 ..	7·1	7·4 ,,	9·9 : 1
,, 30, ,, 2 ..	5·5+	5·7−,,	18·4 : 1
,, 31, ,, 1 ..	10·5	10·5 ,,	7·1 : 1
September 5 ,, 1 ..	4·8	5·2 ,,	17·7 : 1
,, 5 ,, 2 ..	5·4	5·3 ,,	14·9 : 1
,, 5 ,, 3 ..	12·4	12·2 ,,	6·2 : 1
,, 5 ,, 4 ..	9·7	9·7 ,,	8·6 : 1
,, 6 ,, 1 ..	10·2	10·3 ,,	7·1 : 1
,, 6 ,, 3 ..	10·1	10·1 ,,	7·2 : 1
,, 7 ,, 2 ..	17·2	17·3 ,,	4·5 : 1
,, 7 ,, 1 ..	13·3	13·9 ,,	5·2 : 1

The results are so grouped around 100 per cent that the method is shown to be practically accurate—certainly for technical analysis. It will be noticed, however, that the tendency is to find more nitrous oxide than was taken; or, in other words, the contraction after running the gas over potassium hydroxide was greater than it should have been. From some later work, an account of which will appear in the communication to follow, I have found that the presence of a fraction of a drop of water in the grisoumeter causes striking results. The water is vaporised by the heat of the glowing spiral, and a reaction takes place by which the water is decomposed, the oxygen uniting with the carbon monoxide to form carbon dioxide, and the hydrogen going free. This causes an increase in the volume of gas after combustion, which does not take place in the absence of an excess of water vapour

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* Hempel, *Berichte*, 1882, p. 910.

† For description, see Hempel's "Methods of Gas Analysis," translated by Dennis; Macmillan, 1892, p. 236.

above that which is necesary to saturate the gases. The reaction is probably expressed by the following:*—

$$CO + H_2O = CO_2 + H_2.\dagger$$

On running the gases over potassium hydroxide, the carbon dioxide formed in this reaction is absorbed with the carbon dioxide formed from the oxygen of the nitrous oxide; but in the reaction with the water, for every volume of carbon monoxide transformed into carbon dioxide, and thereby rendered absorbable, there is a volume of hydrogen left which exactly replaces it, so the result comes out even. The hydrogen set free in this reaction may possibly unite with the nitrogen set free by the reduction of the nitrous oxide, and ammonia may be formed, as in the experiments with hydrogen; or, indeed, other condensation products may be formed. At the time these experiments were made I was not aware of this reaction between carbon monoxide and water, so that I did not note whether or not a fraction of a drop of water had gotten into the grisoumeter. In some experiments, however, I know this to have been the case, for after a partial combustion or an explosion I would run the gases over the potassium hydroxide, and after running them into the burette would then pass them back into the grisoumeter for a second combustion. In these instances I always got a small amount of the potassium hydroxide solution in the top of the capillary of the measuring burette, and sometimes a small particle of the liquid would be carried into the grisoumeter. I think it more than likely that working with a grisoumeter which thus contained an excess of moisture will account for the tendency of some results to come about 0·1 c.c. or more too high, while hardly any fall below.

One very great advantage of this method is that when the amount of nitrous oxide is small, it may be diluted with a large amount of carbon monoxide for convenience of manipulation, and still give good results from combustion. The most satisfactory results and the smoothest and quickest reaction is obtained when approximately,—

$$CO : N_2O :: 7 : 1.$$

If there is less carbon monoxide the mixture explodes, and when the excess of carbon monoxide is large it takes a longer time for complete combustion. It is always best to give a combustion of at least three to five minutes. Unless excess of moisture be present there are no side reactions, and no evidence of condensation products even after a combustion of an hour.

The experiments referred to in the present communication were carried on in the Hoagland Laboratory of Brooklyn, and at the Physiological Laboratory of the Johns Hopkins University during my connection with those laboratories. In addition to this, through the courtesy of Professor Morse, I was able to avail myself of the facilities of the Chemical Laboratory of the Johns Hopkins University, and through the courtesy of Profs. Dennis and Orndorff of Cornell University, I was invited to make use of the facilities of their laboratories while spending my vacation at Ithaca. It was there that the work was brought to a successful termination. It gives me pleasure to express my obligation to these gentlemen for the said courtesies, as well as for useful suggestions from time to time. I am also indebted to Mr. B. S. Cushman, of Cornell, for much valuable assistance.—*Johns Hopkins University Circular*, xiv., No. 116.

Chemical Society Anniversary.—The Anniversary Dinner of the Chemical Society will be held at the Hotel Métropole on Wednesday, March 27th, at 7 p.m. Fellows who wish to be present are requested to communicate with the Secretaries at Burlington House without delay.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 22nd, 1895.

Capt. Abney, F.R.S., President, in the Chair.

Messrs. W. R. Cooper, J. H. Gardiner, and J. W. Rodger were elected members of the Society.

An abstract of Mr. G. H. Bryan's paper on "*The Mechanical Analogue of Thermal Equilibrium between Bodies in Contact*" was read by Mr. Elder.

After commenting on the difficulty in applying the kinetic theory of gases to the case of two substances in contact which do not mix, the author goes on to describe a system by which the phenomena of thermal equilibrium unaccompanied by diffusion can be explained.

The two substances are represented by two sets of molecules, designated by P and Q. Two parallel planes, A and B, at a small distance apart, are imagined to divide space in three parts. Plane A (to the left of B) is supposed to be permeable to the P molecules, but to repel the Q molecules; whilst B is permeable to the Q set of molecules and repels the P set. The spaces to the left of A and to the right of B are thus entirely occupied by the P and Q molecules respectively. Between the planes both P and Q molecules exist, and therefore have opportunities of colliding with one another, and transferring energy from one gas to the other.

Using generalised co-ordinates, it is shown by Boltzman's method that when equilibrium is attained the mean kinetic energies of translation of the two kinds of molecules are equal, just as in the case of molecules which mix.

Instead of assuming the planes A and B to repel the Q and P molecules respectively, the P molecules may be assumed to be positively electrified, and the Q ones negatively electrified; whilst the planes A and B are maintained at a constant difference of potential. The difference of potential thus assumed is analogous to "contact E.M.F.," whose existence is proved by experiment.

The communication concludes with a development of Prof. Boltzman's paper "On the application of the Determinantal Relation to the Kinetic Theory of Polyatomic Gases," read before the British Association at Oxford.

Dr. Stoney thought the arguments were based on actions depending on the distances of the molecules and the supposition that they were rigid. In his opinion events occur in nature which are not represented by this simple theory, and great reservation should be shown in accepting dynamical problems which leave out of account actions occurring between matter and the ether. In nature nothing was large and nothing was small except relatively. Even molecules might possess infinite detail of structure. Their interaction with the ether must be considered in any complete theory.

Mr. G. V. Yule's paper "On a New Harmonic Analyser," and one by H. N. Allen "On the Electromagnetic Field," were postponed.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Dr. McDonald in the chair.

The sixth meeting of the Society for the present Session was held on February 11th.

Mr. A. Forbes Watson read a paper on "*Argon.*"

He gave a connected account of the circumstances which led to the discovery of the gas, and described the methods by which it had been isolated. Particular attention was paid to the question of ratio of specific heats and to the place which the element could occupy in Mendeleeff's table.

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* Dixon, *Phil. Trans.*, 1884, and *Journ. Chem. Society*, 1886.

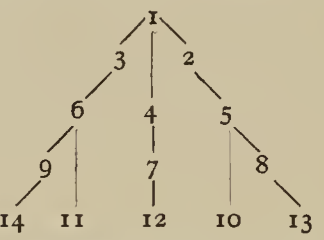
† In my own experiments I have shown the presence of free hydrogen by absorption with palladium.

NOTICES OF BOOKS.

The Genetic System of the Chemical Elements. By W. Preyer. With a Lithographed Table. Berlin: Friedlander and Son. 1894.

The author informs us in his preface that his system includes the families of Mendeleeff's natural system and Lothar Meyer's periodic law, and retains the septimal division first recognised by Newlands. But on considering this system, as well as Wendt's pedigree of the elements and the spiral of Reynolds and Crookes, he finds that some modifications are needed to agree with reality. In his new pedigree of the elements he shows that a series of properties mutually independent are brought into systematic connection. He traces this connection in ten different directions, and hopes that his hypothesis of the derivation of the elements of high atomic weights from those of low ones, and ultimately from an extremely finely divided primitive substance—in fact, protyle—may soon claim the rank of a theory.

He gives the pedigree of the elements according to the following scheme, including fourteen gradation numbers.



Here 1 signifies any one of the seven elements following upon hydrogen in a series arranged arithmetically according to the atomic weights, and at the same time divided into periods of seven members. These elements have been produced according to hypothesis by one condensation. Hence,—

1. Li, Be, Bo, C, N, O, F.

Each of these seven elements, which form the first stage of condensation and represent the first generation in the pedigree, yields on further condensation a second denser stage, *i.e.*,—

2. Na, Mg, Al, Si, P, S, Cl.

Each of the less dense elements 1 underwent a further condensation, forming the elements—

3. Ka, Ca, Sc, Ti, Va, Cr, Mn.

A corresponding process of condensation is carried on through five generations, and thus the author includes in his complete system all the known elements and fifteen which are probable.

Professor Preyer seeks the evidence for his hypothesis in the atomic weights, in the differences of the atomic weights, in the specific gravities, the atomic volumes, the specific heats, the atomic heats, the volume heats, the electro-chemical tensions, the magnetic phenomena, and in valence. Many of the attributes in certain elements have not been determined with satisfactory accuracy. But we may admit that the general consensus of the evidence adduced seems favourable to the views of Prof. Preyer.

Treating of the unknown elements, the author places their number, as an outside estimate, at fifteen. Their properties are, of course, a matter of conjecture. We find the very justifiable remark that all the specimens used for the determination of such points must be absolutely pure. In this respect there is room for delicate and accurate research enough to engage the life-time of not a few zealous and well qualified experimentalists. To such investigations we beg to draw special attention.

Cod Liver Oil and Chemistry. By F. Peckel Möller, Ph.D. London: Peter Möller, 43, Snow Hill, E.C.; and at Christiania, Norway.

This curiously entitled work consists of parts which do not exactly appeal to the same class of readers.

The first portion, paged with Roman numerals, addresses mainly the pharmacist and the physician.

The second and larger section, paged in the ordinary Arabic numerals, claims the attention of the pure chemist.

Into the consideration of the first part we can scarcely enter. We may, however, note that, among the fishes of the Norwegian coast, the halibut has been overlooked, though it reaches an immense size, and, save for the production of oil, it far surpasses the cod. The dangers of the Lofoten fishery are serious. It is here recorded that some years ago 500 fishermen perished in a single day!

In the history of the cod-liver oil trade an epoch has been made by the introduction of the extraction by steam, due to Peter Möller, in 1853.

It is clearly and truthfully shown that the natural colour of cod-liver oil is a very pale yellow, and that the brown qualities, light or dark, owe their colour to decomposition. The most recent improvement devised consists in performing the extraction process in a current of carbonic acid gas, atmospheric air, and consequently oxygen, being excluded. The rancidity of the brown oils is now proved to be due not to free acids, but to the formation of hydroxy-acids. It is interesting to note that persons interested in the brown oil trade calmly assert, in the face of all evidence, that the colourless oils have been artificially bleached. Dr. Möller gives the conditions to be observed if an ideal oil is to be obtained. One of these is that the livers should be perfectly fresh. This is the reason why the Norwegian oils are superior to all others. At the Lofotens the cod are caught close to land, and can be conveyed to the factories before putrefaction has set in. This is not, *e.g.*, the case off Newfoundland.

The purely chemical portion of Dr. Möller's book bears the title—"The Law of Atomic Linking Diagrammatically Illustrated." It is, in fact, a treatise on organic chemistry expressed in graphic formulæ to a most unusual degree. His formulæ showed him why the attempt to form antipyrine by causing a derivative of butyric acid to react upon phenylhydrazin was a failure; the product being, in fact, iso-antipyrine. Another novel view relates to the difference between uric acid and xanthine. Both these substances may be looked upon as consisting of two mols. of urea and one of acrylic acid. The difference between them is that in the one case the acrylic acid turns its extremities towards the urea in a different manner to the other.

Of more importance is the suggestion put forward to explain the rotation of polarised light. Like Baeyer, he is not satisfied with the banal explanation of this phenomenon by the presence of a non-symmetric carbon. The author's own hypothesis does not well admit of statement without the diagrams of succinic acid, dextro-tartaric acid, lævo-tartaric acid, and meso-tartaric acid.

The only objection which we can find to Dr. Möller's method of expounding organic chemistry is that the diagrams which are necessary at every step must be exceedingly costly. If he could find some method of expounding, *e.g.*, his views on the cause of rotatory polarisation without diagrams, his treatise would, we feel sure, be widely read.

The author has little cause to apologise for his English; it is racy, flowing, and idiomatic, enlivened at times with a dry humour which somewhat reminds us of our late friend Dr. Angus Smith.

Action of Picric Acid and the Picrates upon the Mercuric Cyanides. The Isopurpurates.—Raoul Varet.—The author has studied methodically the action of picric acid and of the picrates, on the one hand, upon potassium, sodium, lithium, barium, strontium, calcium, magnesium, cadmium, and zinc cyanides, all of which form isopurpurates. On the contrary, the mercury, copper, and silver cyanides are not decomposed by a solution of picric acid, even if boiling, and they do not yield isopurpurates.—*Bull. de la Soc. Chim. de Paris*, No. 22, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 6, February 11, 1895.

On the presence of Alumina in Plants and on its Distribution.—M. Berthelot and G. André.—The determinations given by the author show that alumina may exist in the ash of annual plants provided with plentiful and deep roots. Its proportion in the analysis of other lucern is comparable to that of the other bases; it coexists with phosphoric acid. But immediately after its absorption (or fixation) by the roots it is arrested. It arrives at the leaves only in a minimum proportion, and in the case of a tree, such as the lime, in a proportion almost infinitesimal. Alumina, as well as aluminium phosphate, may be kept in solution and then absorbed in presence of citric and tartaric acids.

Preparation and Properties of Titanium.—Henri Moissan.—(See p. 103).

Report on a Memoir by E. Hardy relating to the Application of Sonorous Vibrations to the Analysis of two Gases of Different Specific Gravities.—In detecting the proportion of "fire-damp" contained in the air of a coal mine, E. Hardy makes use of a purely physical property, the decrease of sp. gr. which air undergoes in consequence of an admixture of fire-damp. The method is founded on the fact that any variation in the density of a gas feeding a sounding-pipe is shown by a variation in the pitch of the sound produced. As this variation in pitch becomes very sensible by the production of beats, Hardy utilises it for determining the volume of the fire-damp (formene) by means of an apparatus which he names the *formenophone*. It is necessary to exclude from the specimens operated upon all carbonic acid and watery vapour. The Commissioners express themselves perfectly satisfied with the memoir as showing the way for a continuous and systematic record of the proportion of fire-damp present in the air of a mine.

Lowering of the Freezing-points of Dilute Solutions of Sodium Chloride.—A. Ponsot.—This memoir requires to be accompanied by the table and the diagram here given.

Gold Sulphide.—A Ditte.—This paper will be inserted in full.

Method for Determining the Crystallisation of Precipitates. Zinc and Manganous Sulphides and Copper Hydroxide.—A. Villiers.—This memoir also will be inserted in full.

Cinchonigine: Dimorphism of a Compound presenting Specific Molecular Rotatory Power.—E. Jungfleisch and E. Léger.—The two forms of cinchonigine are easily converted into each other. The klinorhombic form is stable at the ordinary temperature, whilst the orthorhombic form is stable at the boiling temperature of ether, about 35°. Except strontium acid tartrate, cinchonigine is the first instance of a dimorphous substance possessing a specific molecular rotatory power.

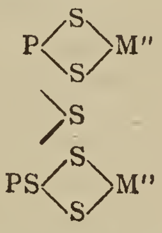
Plurality of Chlorophylls. A second Chlorophyll isolated in Lucern.—A. Etard.—A given vegetable species may contain several chlorophylls. It is convenient to give to each of these pigments isolated chemically a name derived from the botanical name of the plant with an index. Lucern contains among other chlorophylls, medicagophyll-α, $C_{28}H_{45}NO_4$, and medicagophyll-β, $C_{42}H_{63}NO_4$. Certain chlorophylls soluble in pentane are, by their scission, the instruments of the chemical production of essences and oils. Others, insoluble in carbides, tend, on splitting up, to produce carbon hydrates, tannins, and extracts.

Comparison between the Coloured and the Colourless Derivatives of Hexamethyltriamidotriphenylmethane.—A. Rosenstiehl.—In a former paper we have considered three colouring matters and eleven colourless substances all containing the group $[(CH_3)_2NC_6H_4]_3{\equiv}C$, which we represent more simply by $A_3{\equiv}C$. The colourless bodies are divided into two classes, according as they are or are not convertible into colouring matters by means of double decomposition. The coloured substances are characterised by the presence of a negative radicle Cl,I (or, in general, of an acid radicle) united to a methanic carbon. With the latter they have in common an amidised phenylic group in para which satisfies the three other valences of the methanic carbon. In this group the nitrogen is not saturated, but has the function of a trivalent element.

On an Ether of a New Genus. Methylene Lactate.—Louis Henry.—This is a colourless liquid, mobile, of a strong odour, resembling that of methanal and of an extremely pungent taste. Its sp. gr. at 2·5° = 1·1974. It boils at 153—154° under a pressure of 754 m.m. Its vapour-density is 3·47. Its melting-point is −28°. It is insoluble in cold water, but in hot water it dissolves with decomposition.

Bulletin de la Société Chimique de Paris. Series 3, Vols. xi.-xii., No. 22, 1894.

New Series of Sulphophosphides: the Thiohypophosphites.—C. Friedel.—The author describes the iron, aluminium, zinc, copper, lead, silver, mercury, stannic and stannous compounds of the acid. As the general formula of these salts he gives—



Action of Thionyl Chloride upon the Oxalic and Formic Acids.—Ch. Moureu.—Thionyl chloride reacts upon the oxalic (oxalates) and formic acids in the manner of sulphuric acid; that is, as a dehydrating agent, passing itself to the state of sulphurous and hydrochloric acid (or chloride).

Action of Thionyl Chloride upon the Aldoximes. Formation of Nitriles.—Ch. Moureu.—We see that thionyl chloride when reacting upon the aldoximes behaves like acetic anhydride; it withdraws from these substances 1 mol. of water, and yields nitriles according to the general equation—

$$R-CH=NOH+SOCl_2=SO_2+2HCl+R-CN.$$

Determination of Mannite in Wines.—J. A. Müller.—This paper will be inserted in full if practicable.

Synthesis of Selenised Aromatic Compounds.—C. Chabre.—A controversial paper in reply to the strictures of Kraft and Vorster.

Determination of Phosphorus in Products of the Metallurgy of Iron.—P. Benazet.—Certain portions of this extensive paper will be inserted in full.

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Evaporative Power of Coal.—Can any of your readers give me a short and simple receipt for arriving at the evaporative power of a given quantity of coal, say 1 cwt.? Can anyone suggest a work treating on this point plainly?—Subscriber.

Erratum.—P. 79. col. 2, line 20 from top, *for* "hydrogen" *read* "hydrazine." Line 30, *for* "A .. −137°" *read* "A .. −187°."

MEETINGS FOR THE WEEK.

Monday, 4th.—Society of Chemical Industry, 8. "The Durability of Pigments derived from Coal-Tar," by A. P. Laurie, F.C.S. "The Hermite System of Sewage Purification," by Sir Henry Roscoe, F.R.S., and Joseph Lunt, B.Sc.

Tuesday, 5th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
—— Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Society of Arts, 8. "Colonies and Treaties," by Sir Charles M. Kennedy, C.B.

Wednesday, 6th.—Society of Arts, 8. "Cider," by C. W. Radcliffe Cooke, M.P.
—— Institution of Mining and Metallurgy, 8. Discussion on "Some Improvements in Gold Extraction. Followed by Papers.
—— Geological, 8.

Thursday, 7th.—Royal, 4 30.
—— Royal Society Club, 6.30.
—— Royal Institution, 3. "Three Periods of 17th Century History—I. The Stuart Monarchy," by Samuel Rawson Gardiner. M,A.
—— Chemical, 8. "Dimethylketohexamethylene," by Dr. Kipping.

Friday, 8th.—Physical, 5. Exhibitions—By Mr. Nabir, of a Voltameter. By Dr. G. Johnstone Stoney, F.R.S., The Focal Heliostat; An Improvement in Siderostats. "On a New Harmonic Analyser," by G. V. Yule. "On the Electromagnetic Field," by H. N. Allen.
—— Royal Institution, 9. "The Physical Work of Von Helmholtz," by Prof. A. W. Rücker. M.A., F.R.S.
—— Astronomical, 8.
—— Medical, 7. (Annual Dinner).

Saturday, 9th.—Royal Institution, 3. "Waves and Vibrations,' by Lord Rayleigh, F.R.S.

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THE CHEMICAL NEWS.

Vol. LXXI., No. 1841.

NOTE ON THE SPECTRUM OF ARGON.*

By H. F. NEWALL.

In the course of a spectroscopic investigation in which I have been for some time past engaged, a line spectrum, which so far as I was able to make out, was unknown, has frequently presented itself upon my photographs. It appeared in May and June, 1894, under conditions which led me to call it, for the sake of convenience, "the low-pressure spectrum." After their announcement at the Oxford meeting of the British Association, it seemed for many reasons natural to borrow the first letter of Lord Rayleigh's and Professor Ramsay's names to give to the unknown lines, and in the measurements of the photographs which showed the lines well there appears an "R" against seventeen lines out of sixty-one measured, the remaining lines being known to belong to Hg, H, N, and nitrocarbons. It transpires now, as I learnt from reading the abstract of the paper in which Lord Rayleigh and Professor Ramsay describe their consummate researches on argon, that the symbol "A" should have been used instead of "R" to designate the lines on my photographs. For the lines are argon lines.

The conditions under which the spectrum of argon has appeared in my investigations are of interest at the present time, and I hope a description of them may not be unacceptable.

A glass bulb was sealed hermetically to a mercury pump of the Hagen-Töpler form, in which there was strong sulphuric acid floating on the surface of the mercury. The bulb was exhausted as low as possible and refilled with air. The pressure was reduced to about 180 millionths of an atmosphere (=0·14 m.m.), at which pressure a bright discharge could be passed through the residual gases by means of Professor J. J. Thomson's method of surrounding the bulb by a coil of wire, which carries a very rapidly alternating current produced by the discharge of a condenser.

The discharge was passed for thirty minutes, during which time a photograph of the spectrum was taken. The pressure of the gas in the bulb fell during the passage of the discharge from the value 174 M (=0·13 m.m.) to 112 M (=0·085 m.m.), The spectrum shows the bands of nitrogen strong, also mercury lines and nitrocarbon groups strong, hydrogen weak, no oxygen or argon.

Again the discharge was passed for thirty minutes and a new photograph was taken. The pressure fell from 100 M (=0·076 m.m.) to 20 M (=0·015 m.m.); the nitrogen spectrum had faded considerably, and there had appeared a number of fine lines which I was unable, in spite of careful efforts, to identify with the lines of any known substances.

The nature of my method of investigation of spectra is such that it is not difficult to pick out of the numerous spectra which appear superposed on the photographic plate the lines which belong to any one spectrum. (The photographic re-productions attached show clearly the ease with which this may be done).

The results of measurement made in the last few days of seventy-two lines in my "low-pressure spectrum" are given below, and side by side are given the measurements of the wave-lengths determined by Mr. Crookes for the argon lines.

The agreement of the measurements shows conclusively that we have been measuring the same spectrum. Be-

TABLE OF WAVE-LENGTHS.

H. F. Newall.		William Crookes. Jan. 24, 1895. *The Two Spectra of Argon.*			
Measurements of lines on photograph.		Blue.		Red.	
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Inten.
4879·8	5	487·9	10	487·9	4
4847·2	5	484·75	1		
4808·0	9	480·50	7		
4766·6	5	476·30	1		
4738·0	8	473·45	6		
4729·4	6	472·66	2		
				470·12	8
4659 6	7	465·65	5		
4644·0	1				
4639·0	2				
4632·1	4			462·95	5
4611·0	9	460·80	8		
4592·0	8			459·45	2
		458·69	6		
4581·2	6	457 95	6		
4546·5	7	454·35	7		
				451·40	2
		450·95	8	450·95	9
4482·2	6	447·83	6		
4460·0	2				
4431·3	10	442·65	10		
4426·0	10	442·25	10		
4421·2	4				
4414·1	4				
4401·7	9	439·95	10		
4400·1	5				
4379·8	8	437·65	9		
4375·8	3				
4370·4	8	436·90	9		
4351·4	7	434·85	10		
4336·0	2			434·50	5
4330·8	10	433·35	9	433·35	9
4308·7	4			430·05	9
4299·4	4	429·90	9		
4282·1	6				
4277·4	8 ? N	427·70	3		
		427·20	7	427·20	8
4266·4	9 ? N	426·60	6	426·60	4
		425·95	8	425·95	9
		425·15	2	425·15	3
4227·5	8	422·85	6		
CN group has, though only of intensity 5, obliterated this set of lines.		420·10	10	420·10	10
		419·80	9	419·80	9
		419·15	9	419·15	9
		418·30	8	418·30	8
		416·45	8	416·45	4
		415·95	10	415·95	10
4155·8				415·65	6
4130·9	6	413·15	3		
4104·2	8	410·50	8		
4082·2	4				
4075·8	3				
4072·4	9	407·25	8		
4069·7	2	404·40	8	404·40	9
4042·7	5				
4038·2	5				
4035·0	2				
4033·7	3	403·30	1		
4013·8	8	401·30	8		
3994·8	6				
3991·3	4				
3979·2	3	397·85	1		
3973·0	4				
3968·0	7	396·78	3		
		394·85	9	394·85	10
3944·1	5	394·35	3		
3932·3	5				
3930·8	3	393·18	3		

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* A Paper read before the Royal Society, February 21, 1895.

Measurements of lines on photograph.		Blue.		Red.	
Wave-length.	Intensity.	Wave-length.	Intensity.	Wave-length.	Inten.
3928·2	8	392·85	9		
3920·3	6				
3918·8	5	392·75	3		
		391·50	1		
3892·2 ?	—			390·45	8
3883·2	5	389·20	5		
3873·4	4	387·55	2		
		387·18	2		
3868·1	6	386·85	8		
3850·8	7	385·15	10		
		384·55	1		
		383·55	2	383·55	3
3827·0	—	382·75	2		
3809·8	4	380·95	4		
		380·35	1		
		379·95	1		
3781·8	6	378·08	9	377·15	1
		377·05	2		
3766·1	5	376·60	8		
3750·2	3				
3738·8	3	373·85	3		
3730·0	8	372·98	10		
3719·2	2	371·80	4		

tween Hγ and wave-length 370, the agreement is all that we could hope for, taking into account the fact that my measurements were not made with a view of giving a final and carefully-considered set of measurements of wave-lengths, but between Hγ and Hβ there is a systematic difference of about 3 tenth-metres, which I am unable at present to account for. The agreement of grouping and intensity, however, leaves no doubt as to the identity of the spectrum of my low-pressure lines with the spectrum of argon. I have reduced my measurements with reference to Rowland's scale of wave-lengths, and I infer from the value adopted for the Hβ (F) line that Angström's scale has been used in Mr. Crookes's reduction. The difference between the scales is not enough to account for the discrepancies above referred to.

The experiments were repeated, with slight variations, several times, with results which, so far as the spectrum of argon is concerned, were constant. But it was noted that continued passage of the discharge appears to result in the attaining of a certain minimum pressure, after which there is slight and slow rise to a tolerably-fixed pressure. It is not necessary to dwell on these points in the present note.

It is interesting to find argon asserting itself, unsolicited, in quite new circumstances, and under conditions which practically constitute one more mode of separating argon from nitrogen—namely, the getting rid of nitrogen by passing electric discharge through it in the presence of hydrogen or moisture and acid.

REMARKS ON THE ATOMIC WEIGHTS.

By LECOQ DE BOISBAUDRAN.

For a long time I have been engaged in studying the relation among the atomic weights of the elements, and if I have not yet published my attempt at the classification of the simple substances it is because this investigation presents great difficulties, and because errors are easily committed. We sometimes meet with interesting relations on classifying the elements according to systems which are not merely different, but incompatible.

Such as it was some years ago, it gave me the atomic weight of gallium with a very satisfactory exactitude, and it has enabled me to modify happily the atomic weight of germanium, which had then been provisionally determined by Prof. Winkler upon a specimen which was imperfectly purified.

These two successes will, I hope, serve as my excuse to the Academy if I venture to submit to it certain deductions from my theory which seem to connect themselves with the question of argon.

This substance, so brilliantly discovered by Lord Rayleigh and Prof. Ramsay, may perhaps take its place in a family of elements no member of which is hitherto known.

This family, whose existence my classification enables me to assume should be of a non-metallic nature, and should comprise elements having the atomic weights—20·0945; 36·40 ± 0·08; 84·01 ± 0·20; 132·71 ± 0·15, if we assume arbitrarily O = 16.

The atomicity of the new family should be even (octo-atomic), but its component elements should be devoid of the faculty of combining with other elements.

The bodies 20·0945 and 36·40 should be relatively abundant in Nature, but 84·01, and especially 132·71, should be rare.

The element 36·40 should be more volatile than sulphur, and the element 20·0945 more volatile than oxygen. Lastly, the elements 84·01 and 132·71 should be respectively more volatile than selenium and tellurium.

At the moment of presenting this note to the Academy I read, in the *Revue Generale des Sciences*, the memoir of Lord Rayleigh and Prof. Ramsay, and I see that these *savants* have thought of attaching argon to the eighth rank in the classification of Mendeleeff. It seems to me that they are perfectly right. The considerations according to which I have presupposed the existence of a new family, non-metallic and octo-atomic, are not the same as those which have led Prof. Mendeleeff in his classification, but they are far from being contradictory. These are different points of view which enable us, I believe, to see different aspects of the same truth, and each of which presents special advantages.

My classification claims the advantage of permitting a calculation of the atomic weights, exact or closely approximate.—*Comptes Rendus*, cxx., p. 361.

HOW TO PREPARE ARGON ON A LARGE SCALE.

By BOHUSLAV BRAUNER, Ph.D.,
Late Bishop Berkeley Fellow of Owens College.

I have not yet ceased to study Lord Rayleigh's and Dr. Ramsay's paper on Argon, and I well consider the difficulties connected with the isolation of that new gas. A hard work of more than one week is necessary to obtain half a litre of the gas, *i.e.*, 1 grm. (560 c.c. weigh 1 grm.).

The method of diffusion was tried by the authors for an accumulation of the gas, but it does not seem to be promising much. I think the reason is this :—

The rate of diffusion of gases is inversely proportional to their molecular weight. Now the molecular weight of argon is A = 40 when O = 32 and N = 28, and the theoretical coefficients of diffusion will be A = 0·894, O = 1·000, N = 1·069. These numbers differ enough as to promise a good result, and yet they will hardly be confirmed by experiment, for the following reason :—

Argon *is*, or at any rate behaves physically as, a monatomic gas, and we must therefore suppose that its single atoms will pass more easily through the pores of membranes than would correspond to its calculated diffusion coefficient, and that it will meet, on its passage through the pores, with far less obstacles than a diatomic or polyatomic gas molecule of the same weight, owing to the greater distance of atomic centres in the latter. It will be, therefore, only slightly more accumulated in the air which has *not* diffused through the churchwarden tobacco-pipes—as proved by experiment. Of course it must be considered that the unknown *coefficient of transpiration* plays an important *rôle* at the same time.

A much better result might be expected from the property of argon, being 2½ times more soluble in water than nitrogen (Rayleigh and Ramsay). Large quantities of argon will be needed for the complete study of its physical, chemical, and physiological (biological) properties, especially of its behaviour against organisms (repetition of Priestley's work from a modern point of view) and micro-organisms, as pointed out by Berthelot and the author of the present lines simultaneously. This is all impossible, unless it becomes practicable to prepare argon on a large scale.

Let us consider the following:—

In the year 1870, Mallet (*Dingl. Pol. Journ.*, 199, 112; *Journal fur Gasbereitung*, 1870, 538) had established an industrial method of preparing oxygen from the atmospheric air upon the property of water of absorbing oxygen more eagerly than nitrogen. By means of the apparatus described (*loc. cit.*) air is pumped into water under large pressure; the absorbed gases are liberated, and pumped again into water. After repeating this process eight times, a gas is obtained which consists of 97·3 parts of oxygen and 2·7 parts of nitrogen.*

I have no doubt that this last is nearly pure, or at least highly accumulated argon, and that this method will prove effective for the production of "crude argon," especially if oxygen be removed first,—*e.g.*, only technically,—by passing the air over red-hot iron turnings.

I know the munificence of rich intelligent Englishmen, and I think I am not mistaken in supposing that a possessor of chemical works—*e.g.*, the generous supporter of chemico-physical research, and founder of the "Davy-Faraday Research Laboratory"—would be able to establish a plant for the production of "crude argon" on a large scale, on the above plan, and store it in Brin cylinders, which would greatly help the study of one of the most important scientific problems.

Though a "pure scientist" I may be allowed to mention the possible first practical application of argon, which will be undoubtedly for filling Geissler tubes as described by Mr. Crookes. Such articles would find enormous sale amongst the many chemical and physical institutions and laboratories, and the not smaller number of scientific workers and amateurs of the whole world.

I shall be glad if the above lines should prove a step towards the solution of the problem in question.

Bohemian University, Prague,
February 28, 1895.

ACTION OF PHOSPHORUS PENTACHLORIDE UPON α-BENZOYLPHENYLHYDRAZIN.

By H. v. PECHMANN and L. SEEBERGER.

On heating symmetrical benzoylphenylhydrazin with phosphorus pentachloride, the authors obtained, besides the imid-chloride of the latter, a series of compounds which on examination have been chiefly identified as benzoylised hydrazides of phosphoric acid. Among these compounds are—

1. *Chloromethylbenzenphenylhydrazon*,—

$$C_6H_5CCl.N.NHC_6H_5.$$

This compound is characterised by the following reactions:—Insoluble in soda-lye; turned to a blue-green by concentrated sulphuric acid and ferric chloride. An especial characteristic is the formation of red crystalline needles of formazylbenzol if the alcoholic solution is brought in contact with phenylhydrazin at the common temperature.

2. *Lactone of s-Benzoylphenylhydrazid phosphoric Acid.*—This compound has the composition $C_{13}H_{11}N_2PO_3$. It melts at 161°. Readily soluble in alcohol, insoluble in water. Readily taken up by soda-lye. Solution in concentrated sulphuric acid is slowly rendered blue by ferric chloride. Solution in concentrated sulphuric acid does not reduce mercury oxide. A distinction from *s* benzoylphenylhydrazin and—

3. *s-Disbenzoylphenylhydrazido phosphoric Acid*,—

$$C_{261}H_{23}N_4PO_4.$$

This compound crystallises from methylic alcohol in prisms of a vitreous lustre or felted needles; melting-point 131—132°. It is soluble in soda-lye. The solution in concentrated sulphuric acid is rendered violet by ferric chloride. The solution in chloroform reduces mercury oxide in the cold (rendering the presence of two imido-groups probable). Hot concentrated sulphuric acid splits it up into phosphoric acid and benzoylphenylhydrazin.

4. *Lacton of s-Disbenzoylphenylhydrazido-phosphoric Acid.*—This compound, $C_{26}H_{21}N_4PO_3$, is insoluble in soda-lye. The sulphuric solution is slowly turned red by ferric chloride. If boiled with glacial acetic acid, is split up into phosphoric acid and benzoylhydrazin. The solution in chloroform does not reduce mercury oxide.

5. On heating *s*-benzoylphenylhydrazin with phosphorus pentachloride for some hours, a compound is obtained which is not yet named. Its composition is probably similar to that of No. 4. It contains 11·8 per cent N and 7·0 per cent P. It melts at 220°. Insoluble in soda-lye. Solution in concentrated sulphuric acid is gradually turned red by ferric chloride. Permanent with mercury oxide.—*Berichte*, xxvii., p. 2123.

THE ACTION OF PHENYLHYDRAZIN UPON ETHOXYMETHYLENMALONIC ETHER.

By L. CLAISSEN and C. HAASE.

Malonic ether combines easily with orthoformic ether to ethoxymethylenmalonic ether.

We have treated this ether with phenylhydrazin, and ultimately arrived at phenylpyrazolon, with the melting-point 118°. A discussion on the constitution of this substance has arisen between Stalz, von Rothenburg, and Ruhemann and Morrell. Stalz regards the substance fusible at 118° as (1)-phenyl-(5)-pyrazolon, and that fusible at 153° as (1)-phenyl-(3)-pyrazolon, whilst the conclusion of von Rothenburg is exactly opposite. From what follows we are compelled to accept the view of Stalz as correct.

1. *Phenylhydrazid or Phenylhydrazon*, when purified, melts at 112°; it dissolves easily in alcohol, acetone, benzene, chloroform, and acetic ether, but less readily in alcohol. Its composition is $C_{14}H_{18}N_2O_4$.

2. *Phenyl-(5)-pyrazolon-(4)-carbonic Ether.*—Its sodium salt crystallises from hot water in fine shining needles. From its aqueous solution acetic acid throws down pyrazolon carbonic ether as a white precipitate. After drainage we dissolved it in hot alcohol, and added water to incipient turbidity. After standing for some time and evaporation, the ether separated in long white silky needles, fusible at 117—118°. It is slightly soluble in water, readily soluble in alcohol, ether, acetone, and benzene. The alcoholic solution is coloured a deep red by ferric chloride.

3. (1)-*Phenyl-(5)-pyrazolon-(4)-carbonic Ether.*—Its percentage composition is—

C	58·82
H	3·92
N	13·73

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* On representing the decrease of the percentage of oxygen after each operation *graphically*, a curve is obtained, which shows clearly that after several operations the absorption coefficient of "atmospheric nitrogen," which is then rich in argon, approaches that of oxygen.

It melts at 92—93° with an escape of gases. It is distinguished from the very stable (1)-phenyl-(5)-pyrazolon-(3)-carbonic acid of Wislicenus by the readiness with which it splits off carbonic acid on boiling with water, or more closely on keeping. This instability of the acid depends on the position of the carboxyl group, which occupies a place similar to that in acet-acetic acid.

4. (1)-*Phenyl*-(5)-*pyrazolon* may be obtained directly from the carbonic ether by dissolving it in so much soda-lye that to each mol. of the ether there are present at least 3 mols. of soda-lye. The solution, after being heated for some hours on the water-bath, is precipitated with hydrochloric acid, and then heated until the escape of carbonic acid has ceased. As it cools, the pyrazolon deposits as a white mass. After purification it crystallises in colourless flat prisms, melting at 118—119°. The pyrazolon has the composition $C_9H_8N_2O.HCl$. In its behaviour it agrees completely with Knorr's (1)-phenyl-(3)-methyl-(5)-pyrazolon. With ferric chloride it gives Knorr's pyrazol-blue reaction very distinctly. This reaction is best obtained by dissolving a very little pyrazolon in a few c.c. of boiling water, and carefully adding to the hot solution a very dilute solution of ferric chloride (at most 4 per cent). The blue obtained from the above pyrazolon is of a more violet shade than that from phenylmethylpyrazolon.

The above pyrazolon yields with benzaldehyd a benzal compound; with nitrous acid an isonitroso-derivative. The former forms reddish yellow flattened needles, melting at 170°. The isonitroso-compound crystallises in tender needles of an orange colour, which melt at 160° with decomposition.

The authors conclude their paper with a full discussion of the structural formulæ which have been proposed for pyrazolon, and ascribe the preference to that of Stalz.—*Berichte*, xxviii., No. 1, p. 35.

ON THE

PHOTOGRAPHY OF THE LIGHT RAYS OF THE SMALLEST WAVE-LENGTHS.*

By Dr. VICTOR SCHUMANN.

At the conclusion of my investigation on the photography of the luminous rays of the shortest wave-lengths (presented to the Imperial Academy of Sciences of Vienna in the year 1893), I promised as a continuation the solution of several problems there specially indicated. As the preliminary researches commenced a year ago already afford a series of facts ripe for mention, I permit them to follow in as far as they relate to the rays of the shortest wave-lengths. A complete report on the entire results, along with the figures of the spectra obtained, will at no very distant date complete my present communications.

1. I have improved my ultra-violet sensitive plate and the process for its production so far that its sensitive coating may be produced in half an hour; that it works more sensitively and neatly than the former plate, bears the most powerful developers without injury, and can be made still more sensitive for the ultra violet by immersion in common water.

2. My vacuum spectrograph, after a modification recently undertaken, effects, whilst the sharpness of the spectra remains faultless, more in a few minutes than previously in hours.

3. The spectrum of hydrogen taken with my improved spectrograph and the new plate displays, as compared with former proofs, a further important increase in length.

4. The same holds good for the spectra of Fe, Co, Al, Zn, Cd, which previously extended only to the wave-length 170 $\mu\mu$. They are now but little inferior in extent to the spectrum of hydrogen. I have not yet been able to examine other spectra in this respect.

5. The limit of the spectrum above named, drawn close upon 170 $\mu\mu$, was a consequence of the impervious character of the air and of the vapour of the electrodes. The air only has been latterly found to be a little more transmissive than I formerly felt justified in assuming, but even in strata of very slight thickness (a few hundredths of a m.m.) it interferes to a great extent with the photographic action of the most refrangible rays. I have been able to trace its absorbent influence to far below a stratum of 0·01 m.m. in thickness.

6. Hydrogen in a dense layer visibly absorbs the most refrangible rays, and still more if imperfectly dried.

THE ACTION OF MAGNESIUM UPON THE VAPOURS OF THE ALCOHOLS,

AND A

NEW METHOD OF PREPARING ALLYLENE.*

By EDWARD H. KEISER and MARY B. BREED.

Under certain conditions magnesium is one of the most active elements. At high temperatures, as is well known, it has the power of reducing many of the most stable oxides, and in the absence of oxygen it can combine with nitrogen and form a nitride. That magnesium can also unite with carbon and form derivatives of the hydrocarbons will appear from the experiments described in this paper. An exhaustive study of the action of magnesium upon the oxides and hydroxides of the elements has been made by Winkler (*Ber. d. Deutsch. Chem. Ges.*, xxiii., 120, 772, 2642), and Seubert and Schmidt (*Liebig's Annalen*, cclxvii., 218) have studied its effects upon the chlorides of the elements. So far as we know, no one has hitherto examined systematically the action of magnesium upon organic compounds containing oxygen. Preliminary experiments showed us that when magnesium is heated with organic oxygen compounds, such as alcohols, acids, ketones, &c., a reaction, accompanied by an incandescence of the metal, takes place at more or less elevated temperatures. Thus far we have studied in detail the action of the metal upon several alcohols, and, as one of the results, have found a ready method of obtaining the unsaturated hydrocarbon allylene, C_3H_4.

The experiments were conducted as follows:—The magnesium, in the form of filings, was placed in a porcelain or iron boat, and heated in a combustion tube through which the vapour of the alcohol was passed. Before raising the temperature of the magnesium, the air in the apparatus was expelled by the alcohol vapour. At a low red heat the magnesium begins to glow at one end of the boat, and usually, after a few moments, it becomes red-hot throughout its entire mass. The boat and its contents are then allowed to cool down in the alcohol vapour. During the time that the magnesium is glowing, large volumes of gas are evolved from the tube. These gases were in each case collected in a gasometer, and subsequently analysed.

The first alcohol examined was methyl alcohol. The magnesium, at a low red heat, acts energetically upon it. After cooling, the residue in the boat has the appearance of a dark, black, coherent mass. When brought into water, this black residue slowly gives off a gas. If now a drop or two of a solution of ammonium chloride be added, a moderately rapid current of gas is given off. This gas has an odour like that of acetylene, but when it is conducted through an ammoniacal solution of cuprous chloride, the greenish yellow precipitate of cuprous ally-

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* Imperial Academy of Science at Vienna, February 7, 1895.

* Read at the Chemical Section of the Franklin Institute, Dec. 18, 1894.

lide is formed. In an ammoniacal solution of silver nitrate, a white crystalline precipitate of silver allylide is obtained. Both these precipitates, when they are filtered off, washed, and dried, explode if they are heated up to about 150°. When treated with dilute nitric or hydrochloric acids, they dissolve with an evolution of allylene. The silver precipitate can be obtained in pure condition more readily than the copper compound. An analysis of the former gave the following result:—

I. 0·1292 grm. gave 0·1270 grm. AgCl=73·97 p. c. Ag.
Calculated for C_3H_3Ag, 73·45 ,, ,,

The gas which was given off during the time that the magnesium in the porcelain boat was glowing in the methyl alcohol vapour, gave, on analysis, the following results:—

CO_2	0·8
CO	0·6
CH_4	19·7
H	78·9
	100·0

The action of zinc dust upon the vapour of methyl alcohol has been examined by W. Jahn (*Monatshefte*, 1880, i., 378 and 675), who found that the chief products were hydrogen and carbon monoxide. As a by-product, a small quantity of marsh gas was obtained. It is evident, from the above analysis, that the action of the magnesium is essentally different, the carbon monoxide being practically absent in the products obtained when this metal acts upon the methyl alcohol. We have found that another metal, namely iron, decomposed the methyl alcohol vapour in the same way that zinc does. Thus, when the methyl alcohol vapour was passed through a tube containing iron, as, for example, a boat made of thin iron sheet, the alcohol was decomposed into carbon monoxide and hydrogen. An analysis of the gas thus obtained gave the following results:—

CO_2	3·8
CO	26·8
CH_4	1·6
H	67·4
	99·6

In short, when methyl alcohol is passed over heated metals, such as iron or zinc, it is resolved into hydrogen and carbon monoxide; if it be passed over heated magnesium, the chief products are hydrogen and marsh gas.

The next alcohol examined was ethyl alcohol. The action in this case was similar to that described in the case of methyl alcohol. The residue remaining in the boat was treated with water and a few drops of ammonium chloride solution, and the gas that was given off was conducted through a series of bottles containing an ammoniacal solution of silver nitrate. The white crystalline precipitate, on analysis, gave the following percentage of silver:—

I. 0·1163 grm. gave 0·11365 grm. AgCl=73·53 p. c. Ag.
II. 0·0979 ,, 0·09615 ,, ,, 73·89 ,, ,,
Calculated for C_3H_3Ag, 73·45 ,, ,,

In this case, also, allylene is given off when the magnesium residue is decomposed by water. The gases formed during the action have the following composition:—

CO_2	0·0
CO	0·4
C_2H_2	10·0
C_2H_4	4·0
CH_4	11·1
H	72·9
	98·4

The chief constituent again is hydrogen. Carbon monoxide is practically absent, as we should expect, knowing that this gas is reduced by magnesium. Acetylene and marsh gas are present in about equal quantities. Jahn found that zinc dust at low temperatures decomposes ethyl alcohol smoothly into ethylene and water, the latter being reduced to hydrogen by the zinc. At higher temperatures he obtained hydrogen, marsh gas and carbon monoxide, and a trace of acetylene. We have found that iron decomposes ethyl alcohol in very much the same way that zinc does at elevated temperatures. The gas obtained by passing ethyl alcohol over heated iron had the following composition:—

	CO_2	0·5
	CO	8·0
Unsaturated hydrocarbons	$C_2H_2+C_2H_4$	4·0
	CH_4	13·0
	H	63·8
		99·3

Propyl alcohol was examined in the same way. In this case the black magnesium residue is decomposed by water at the ordinary temperature, and the quantity of silver precipitate is very much greater than in the preceding cases. So readily is allylene obtained from propyl alcohol and magnesium by this method, that for the purpose of preparing the gas for experiments on the lecture table it is much to be preferred to the ordinary method of decomposing propylene bromide with alcoholic potash. Analysis of the pure white silver allylide thrown down in the second wash-bottle from the generating flask gave, on analysis, 73·39 per cent of silver.

0·15605 grm. gave 0·1522 grm. AgCl = 73·39 per cent Ag.
Calculated for C_3H_3Ag = 73·45 ,,

The precipitate in the first wash-bottle was not so pure; it evidently contained some silver acetylide. On analysis, 0·20095 grm. gave 0·19985 grm. AgCl, or 74·83 per cent. Silver acetylide contains a higher percentage, namely 89·99 per cent of silver.

An analysis of the gases formed when the magnesium acts upon propyl alcohol showed that in general the action is similar to that which took place in the experiments with ethyl alcohol. The analysis gave these figures:—

CO_2	0·0
CO	3·5
Unsaturated hydrocarbons	17·8
Saturated ,,	19·9
H	57·8
	99·0

The chief products of the decomposition of propyl alcohol, under the action of magnesium, are hydrogen and saturated and unsaturated hydrocarbons, the latter being present in nearly equal volumes. The same alcohol is decomposed by heated iron in a different way, the analysis of the gas having given the following values:—

CO_2	0·6
CO	16·4
Unsaturated hydrocarbons	16·7
Saturated ,,	23·6
Hydrogen	42·7
	100·0

With zinc dust Jahn found that, at low temperatures, propylene and hydrogen are the chief products.

The other alcohols that have been examined are allyl, isobutyl, and amyl alcohols. The first of these, namely, allyl alcohol, is even better than normal propyl alcohol for the preparation of allylene. An abundant precipitate of silver allylide is obtained, and an analysis showed that it was free from silver acetylide.

I. 0·17185 grm. gave 0·16735 grm. AgCl = 73·27 p.c. Ag.
Calculated for C_3H_3Ag = 73·45 „

In this case the precipitate obtained in the first wash-bottle gave on analysis a result which showed that it contained no silver acetylide.

0·16705 grm. gave 0·1620 grm. AgCl = 72·97 per cent Ag.
For C_3H_3Ag = 73·45 „

The ease with which, from a few c.c. of propyl or allyl alcohols and a few grms. of magnesium powder, an appreciable quantity of allylene silver can be obtained, makes this method of preparing allylene much more convenient than the one ordinarily used.

From isobutyl alcohol and magnesium a residue was obtained, which, on treatment with water and ammonium chloride, gave a gas which, besides hydrogen, contained acetylene and allylene, as was shown by the percentage of silver in the silver precipitate.

0·18335 grm. gave 0·18845 grm. AgCl=77·33 per cent Ag.

From amyl alcohol the yield of silver precipitate was not very large, but here also the unsaturated hydrocarbon was allylene.

0·08585 grm. gave 0·08365 AgCl=73·31 per cent Ag.

Other alcohols and organic compounds containing oxygen will be investigated in a similar way.

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.*

By AMOS PEASLEE BROWN.

While much has been done in the way of investigating the chemical properties and constitution of the various artificial chemical compounds, comparatively little attention has been paid to the constitution of the naturally occurring chemical compounds. The carbon compounds, for instance, have in an immense number of cases been investigated with sufficient exactness to allow of our expressing their constitution by means of structural formulæ, but to how many minerals, aside from the simplest compounds, can we assign structural formulæ that are based on any knowledge that we possess of their reactions? It is true that much has been done in the way of the artificial production of minerals, and some knowledge of the constitution of certain minerals has been arrived at by a study of their decomposition products, but very little in comparison to the extent of the field. There are probably several reasons for this neglect of the study of the chemical properties and constitution of minerals, as want of homogeneity in the minerals themselves, difficulty of procuring or separating pure material for investigation, and similar difficulties which do not so frequently occur with artificial compounds. It thus happens that mineral chemistry is not as much studied as it deserves to be. Certain groups of minerals have, however, received some attention; for instance, Professor F. W. Clarke has been carrying on a very interesting series of investigations on the constitution of certain silicates which have been productive of most valuable results. The natural sulphides, sulpharsenides, and sulpho-salts present some very interesting problems in regard to their constitutton, and it was with a view of adding to our knowledge of the chemical behaviour of two of these sulphides that I undertook the series of investigations about to be described.

The compound FeS_2 is found in nature in two well-known forms—the one pyrite (the isometric mineral) and the other marcasite (the orthorhombic mineral). Since the separation of the two names from the general term, pyrites, it has been recognised that the orthorhombic form is lighter in colour and also of lower specific gravity than the isometric form. From early times, also, the greater tendency of “white pyrites,” or marcasite, to decompose in the air was well known.

Pyrite, the form which resists atmospheric weathering most thoroughly, is of a bright brass-yellow colour and metallic lustre, breaking with an uneven conchoidal fracture, but bright on the surface of fracture. It crystallises in the isometric system in forms showing generally pentagonal hemihedrism. Its specific gravity ranges from 4·8 to 5·2, averaging somewhat over 5. The brass-yellow crystals are generally quite unaltered in the air.

Marcasite, on the other hand, has a pale greenish or greyish yellow colour, an uneven fracture, which shows a somewhat fibrous structure, and generally but little lustre on the surface of fracture. It crystallises in the orthorhombic system, very commonly in twins or radiated fibrous masses. It is not very permanent in moist air, but readily decomposes and largely into $FeSO_4$. The chemical formula of either form, calculated from quantitative analyses, is the same, FeS_2 or Fe=46·67 per cent, S=53·33 per cent.

The chemical study of these two minerals has been mainly confined to the formation of one of them artificially and to a few experiments on their relative decomposability. Pyrite has been made artificially in a number of ways; marcasite has not as yet been formed artificially. (Doelter, *Zeit. fur Kryst.*, xi. 31, 1885; cf. Dana, “Syst. Min.,” 1892). In 1836, Wöhler (*Pogg. Ann.*, xxxvii., p. 238) produced cubes and octahedra of pyrite by subjecting a mixture of ferric oxide, flowers of sulphur, and ammonium chloride to a temperature a little above the volatilising point of the ammonium chloride. The resulting mass was washed to isolate the crystals from the accompanying pulverulent matter. Stanislas Meunier (“Les Méthodes de Synthése en Mineralogie, S. Meunier, 1891”) modified this method by mixing equal parts of ferrous carbonate and sulphur and heating in glass tubes over a moderate flame. When the excess of sulphur has been driven off, there remains a black powder containing a considerable percentage of cubes of pyrite. Dana (“System of Mineralogy,” edition of 1868, p. 64) states that pyrite may be made “by slow reduction of ferrous sulphate in presence of some carbonate.” Baubigny (S. Meunier, “Synth. Min.,” p. 279) produced FeS_2 as a crystalline crust by acting on metallic iron by a solution of SO_2 in water (H_2SO_3) in closed tubes and at a temperature of 200°. As neither this experiment nor the one immediately preceding it shows that the crystals were isometric, it is possible that both of them may be marcasite. Henri Sainte Claire Deville (cited in “Dict. Chem.” of Wurtz, by E. Wilm, article “Iron,” i., p. 1414) produced cubes of pyrite by melting a mixture of potassium sulphide (K_2S) and iron sulphide (FeS) in presence of excess of sulphur. This reaction, if correct as to the *cubical* product, is a remarkable one, as I should rather expect marcasite to result under such conditions. Senarmont (S. Meunier, “Synth. Min.,” p. 285) produced FeS_2 by decomposing a salt of iron by an alkaline sulphide at an elevated temperature in sealed glass tubes. The product was an amorphous black powder, not altering on exposure to air and not attacked by hydrochloric acid. This may have been pyrite, as marcasite is readily decomposed by moist air. Rammelsberg (*Jour. fur Praktische Chemie*, lxxxviii., p. 266), in 1862, made FeS_2 pseudomorphs after ferric oxide (Fe_2O_3) by passing a current of hydrogen sulphide over it at a temperature between 100° and a red heat. The product of this reaction would likely be pyrite.

In nature it would seem that in most cases the sulphide of iron first formed is FeS, but probably by action of a ferric salt, or carbonic acid (H_2CO_3), causing a loss in iron, FeS_2 results, and this is almost always pyrite. On the other hand, where ferrous sulphate has been reduced by slow action of decomposing organic matter, the resulting sulphide seems to be generally marcasite, which

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* Read before the American Philosophical Society, May 18, 1894. —From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

if not in crystals may be recognised by its ready weathering to ferrous sulphate ($FeSO_4$). This compound may, however, in many cases, be a mixture of pyrite and marcasite, as much pyrite seems to be. (Compare A. A. Julien, "Decomposition of Pyrite," *Ann. N. Y. Acad. Sci.*, iii. and iv.). These several ways in which pyrite may be formed are of importance as indicating the condition of the iron in the compound, and will be referred to later on.

Equally important as bearing on the constitution of these sulphides are the observations that have been made as to their decomposition under atmospheric agencies. On exposing crystallised pyrite to atmospheric weathering it is generally found that but little, if any, change takes place even in a year's time, while crystallised marcasite, under the same conditions, shows a rapid weathering. The main product of the weathering of pyrite in nature is the compound limonite, $Fe_4O_3(OH)_6$, which occurs in large quantities in nature, evidently derived from pyrite. Its pseudomorphs after pyrite are very common. On the other hand, when marcasite weathers a very large percentage of ferrous sulphate ($FeSO_4$) is formed with a comparatively small percentage of limonite, unless the marcasite decomposes underground and under pressure, when limonite is largely produced (Blum, "Pseudomorphosen," 1843, pp. 197—199). Much of the excess of sulphur with marcasite is changed to sulphuric acid, but with pyrite much remains behind as sulphur. Some comparison of the rate of oxidation of these two minerals in the air is afforded by an examination of specimens in a collection. Here it will be found that most of the pyrite is unchanged, but nearly every specimen of marcasite will show tarnish if no other sign of oxidation, and often a considerable coating of oxide can be seen, or a white efflorescence of $FeSO_4$.

Chemical investigations of these two minerals have been mainly in the way of analysis, but some experiments have been made in the way of studying their relative behaviour towards certain reagents. Before describing my experiments, it will be necessary to briefly mention some of these.

Both minerals are decomposed by a solution of silver nitrate and gold chloride, the decomposition taking place quite rapidly (S. Meunier, "Synth. Min." p. 309). My experiments in this connection are mentioned later.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 21st, 1895.

Dr. Armstrong, President, in the Chair.

Mr. Alexander Cameron was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Herbert William Cook, B.Sc., West Mount, Upton, Macclesfield; Edric Druce, Worleston, Nantwich; H. Loft Haller, 27, Hilda Street, Beverley Road, Hull; George Elliott Shaw, 9, Basing Road, Westbourne Park, W.

It was announced that the following changes in the Officers and Council were proposed by the Council.

As *President*—A. G. Vernon Harcourt, M.A., D.C.L., LL.D., F.R.S., *vice* Professor H. E. Armstrong, LL.D., Ph.D., F.R.S.

As *Vice-Presidents*—Professor Roberts-Austen, F.R.S., and Professor Japp, F.R.S., *vice* A. Vernon Harcourt, F.R.S., and Professor William Ramsay, F.R.S.

As *Ordinary Members of the Council*—Professor Bedson, Mr. B. Brough, Mr. Hehner, and Professor McLeod, F.R.S., *vice* Charles F. Cross, A. G. Green, W. H. Perkin, jun., F.R.S., and John A. Voelcker, Ph.D.

Messrs. Evan Bevan, Bertram Blount, and E. W. Voelcker were appointed to audit the Society's accounts.

The following were duly elected Fellows of the Society:—Herbert Anderson, John Melrose Arnot, David Butler Butler, Francis H. Carr, Thomas Bennett Case, B.A., Tom Crossman, Frederic Weldon Daw, Edward Elliott, Henry Fairrie, Alexander Macfarlane, Herbert Edward Gardner, Henry Tresawna Gerrans, M.A., George Goldfinch, Donald St. John Grant, M.A., M.B., Herbert Grime, Weldon Hanson, Harry Harris, Walter Harris, B.A., Ph.D., Hugh Hastings, John Adams Hatfield, Edward Herbert Hill, Percy Hudson, Edgar Joseph, Richard Ernest Kenyon, B.Sc., George Holman Kingdon, B.A., Patrick Henry Kirkaldy, Arthur Marshall, William Baxter McVey, Robert Meldrum, Harry Edward Niblett, B.A., James Albert Offord, Harry James Powell, Herbert Lewin Robinson, Thomas Chilwell Sharrot, Herbert Frederick Stephenson, Henry R. Le Sueur, B.Sc., Thomas C. Warrington, B.A., David John Williams, Evan Williams, Harry Wilson, Henry Stow Young.

Of the following papers those marked * were read:—

*20. "*The Electromotive Force of an Iodine Cell.*" By A. P. Laurie, M.A.

A cell consisting of a zinc and platinum plate, immersed in a solution of iodine in potassium iodide, gives a definite and constant E.M.F., the zinc being dissolved at the expense of the iodine surrounding the platinum plate. On diminishing the strength of the iodine solution the E.M.F. gradually falls off, the rate increasing as the iodine becomes very dilute; the E.M.F. for a 0·1 per cent solution being 1·460 volts, and for a 0·001 per cent solution 1·369 volts. If potassium iodide free from iodine is used, an E.M.F. of about 1·172 volts is obtained. This value is uncertain, and varies for different platinum wires and at different times for the same platinum wire, the highest value being obtained with a wire boiled in soda, then in nitric acid, then washed, and finally heated white-hot. If this wire, however, is left in the solution it gradually falls in E.M.F. to about the value given above.

On adding a trace of iodine, 0·0001 per cent, the E.M.F. at once rises to about 1·320 volts, the reading differing slightly for different wires, and on increasing the amount of iodine the E.M.F. goes on rising, the readings rapidly approximating until before 0·001 per cent is reached the readings are all the same.

Above this value the E.M.F. rises more slowly, but with regular movements; consequently the E.M.F. becomes a measure of the strength of the solution. The author proposes to use these results for measuring the rate of diffusion of very dilute solutions of iodine, and has made more preliminary experiments with the view of doing this.

On diffusing a solution of 0·01 per cent iodine from a short glass tube, with a platinum wire inserted in the closed end, into a mixture of potassium iodide, and taking readings of E.M.F. every half hour, a very regular curve was obtained showing the gradual diminution of the strength of the iodine solution, and in substituting cadmium for potassium iodide as the solvent, results were obtained so nearly agreeing that apparently the iodine is diffusing independently of the potassium iodide or cadmium iodide molecules. The author is now engaged in trying to measure the actual rate of diffusion, and the relation between the rate of diffusion and the temperature of the solution. Incidentally the results show that determinations of the E.M.F. between metals and solutions require in certain cases to be made with considerable care, if the results are to be of any value.

*21. "*Contributions to the Chemistry of Cellulose.*" By C. F. Cross, B.Sc., E. J. Bevan, and C. Beadle.

In a recent monograph ("Cellulose," Longmans, 1895) the authors have suggested a classification of the experimental facts on this subject, and at the same time have pointed out directions for future research. The present paper is a report of progress of investigation upon these lines. The first part is devoted to generally tracing the analogies of cellulose, as a chemical unit, with the salts, and incidentally the points of sharp distinction between cellulose and starch; the experimental study of these points leads to the conclusion that it is not a polyaldose (or aldosan) of the starch type. The points emphasised are:—1. The resistance to hydrolysis as exemplified by the quantitative regeneration of cellulose from the cycle of reaction involved in the formation and decomposition of the xanthates. 2. "Double salt" reactions of cellulose with zinc salts, and the interaction of the cellulose-zinc acetate with acetyl chloride in the cold (at about 30°) forming acetylated derivatives. 3. The mode of decomposition of these cellulose acetates points to the formula $C_6H_6O(OAc)_4$. 4. Certain electrolytic phenomena of the cellulose hydrates which show that in presence of water cellulose is sensitive to the action of the electric current; the metal of a metallic conductor, taken as the "positive" or anode, is attacked and carried forward in the direction of the current, and deposited in the cellulose in a condition of chemical union.

These points have been worked out in experimental detail, and establish several characteristic features which sharply distinguish it from other "colloidal carbohydrates." The electrolytic phenomena are, however, shown by very various substances, *e.g.*, silk, wool, asbestos, &c. In the later sections of the paper the authors, in collaboration with Claude Smith, give the results of experiments on the special group of "natural oxycelluloses," of which the celluloses of the *Gramineæ* are typical. These researches include (1) studies of germination in relation to the furfural-yielding constituents of the tissues of the seedlings; (2) the further history of the plant, for which special barley plots of the Woburn experimental station were selected. The authors have also investigated the furfural reaction, and determined the proportion of volatile acids (formic and acetic) which are formed as bye-products of the condensation. Progress has likewise been made in isolating the "furfuroids" of these celluloses. Treatment with sulphuric acid of 1·6 specific gravity and dilution with water separates the fibrous cellulose into a normal cellulose (insoluble hydrate) and soluble carbohydrates giving a large yield of furfural (50 per cent), but none of the characteristic reactions of the pentosans. It appears to be now generally admitted that these furfural-yielding constituents of plants are products of metabolism of hexoses and hexosans (Cross and Bevan, *Berl. Ber.*, xxvi., 2520; xxvii., 1061; De Chalmot, *ibid.*, xxvii., 1489), though the question of their identity seems to be still a matter of controversy. The evidence, however, so far is against an indiscriminate classification of these bodies as pentoses and pentosans.

*22. "*The Melting-points of Mixtures.*" By Holland Crompton and Miss M. A. Whiteley.

The authors have determined the melting-points of mixtures containing two organic compounds in various proportions. They come to the following conclusions from the results of these experiments:—

1. In all normal cases of solutions in which on solidification the solvent first of all separates out in the pure state, the relationship—

$$\log s = \frac{\rho}{1·98} \cdot \frac{T - T'}{TT'}.$$

holds. Here s is the number of molecules of the solvent contained in one molecule of the solution, ρ is the molecular latent heat of fusion, and T the melting-point in absolute temperature of the solvent, T′ the melting-point of the mixture or solution.

2. For ρ, the value $1·38\ \Sigma vT$ can be substituted where Σv is a number derived from the valencies of the atoms comprising the molecule (*Proc.*, 1894, 240).

3. In a number of instances the observed melting-points of the mixtures are higher than those calculated by these formulæ, and in such cases the discrepancies may be accounted for by assuming that the pure solvent does not separate out from the solution on solidification, but that a solid solution is formed by union of a certain quantity of the dissolved substance with the solvent.

*23. "*The Volumetric Determination of Manganese.*" By Joseph Reddrop and Hugh Ramage.

The authors have examined a method proposed by L. Schneider (*Journ. Chem. Ind.*, 1888, p. 693), in which the manganese salt is oxidised by bismuth peroxide in presence of nitric acid to permanganic acid. After filtration through asbestos, the permanganic acid is determined by titration with hydrogen peroxide. The best strength of nitric acid is 250 c.c. (sp. gr. 1·2) per litre, but the permanganic acid decomposes in the acid solution, and to prevent this decomposition it is filtered into an excess of hydrogen peroxide, and finally titrated with potassium permanganate. It is shown that the error in Schneider's method is at least 0·6 per cent in the analysis of ferromanganese, and 0·06 per cent in that of steel.

Sodium bismuthate prepared from materials free from chlorine, replaces the bismuth peroxide used by Schneider. It is prepared by fusing soda, basic bismuth nitrate, and sodium peroxide; on washing with water the insoluble compound remains.

The analysis of ferromanganese, spiegel, silico-spiegel, iron, and steel are described in detail, and the accuracy of the method established by experiments on quantities of manganese ranging from 0·1 per cent to 80·7 per cent. In a sample of ferromanganese, they obtained by the ordinary gravimetric method, using ammonium salts and correcting for impurities, 80·63 per cent; by Pattinson's method, 80·70 per cent; by the present method, 80·67 per cent. Chromium, copper, nickel, and cobalt up to 5 per cent, are shown to raise the results but very slightly. Sulphuric acid up to normal strength does not interfere, and may therefore be used to expel hydrochloric acid from solutions in which it has been used in dissolving the sample.

The oxidation, filtration, and titration may by this method be completed within fifteen minutes.

24. "*Bromocamphoric Acid, an Oxidation Product of π-Dibromocamphor.*" By F. Stanley Kipping, Ph.D., D.Sc.

It has recently been shown (Kipping and Pope, *Proc.*, 143, 212) that an optically active π-dibromocamphor, melting at 152—153°, can be prepared by gently heating bromocamphorsulphonic bromide; the further investigation of this dibromo-camphor has already led to interesting results, which are briefly described in this note.

On boiling the π-dibromo-compound with concentrated nitric acid for some hours a part undergoes oxidation, and on cooling and adding water a crystalline product is deposited, together with a pale yellow thick oil.

The crystalline product separates from alcohol in nodular aggregates, and melts at about 217° with decomposition; its melting-point and its origin seemed to point to its identity with the bromocamphoric anhydride (m. p. 215—216°) described by Wreden, and more recently investigated by Rupe and Maull, Auwers and Schnell, and Aschan, but analysis and further examination showed that this was not so. The compound has the composition $C_{10}H_{15}BrO_4$ (found C = 43·2, H = 5·4; Calc. C = 43·0, H = 5·4 per cent); it has an acid reaction to litmus, dissolves freely in cold sodium carbonate solution, and also differs from bromocamphoric anhydride in being only very sparingly soluble in chloroform. For these and other reasons it must be regarded as a *bromocamphoric acid*, structurally isomeric with the as yet unknown bromocamphoric acid from which Wreden's anhydride is derived.

When the acid is gently heated with acetic chloride it is converted into the anhydride $C_{10}H_{13}BrO_3$ (found C = 45·92, H = 5·16; Calc. C = 45·97, H = 4·97 per cent); this compound crystallises very well, melts at 155—156°, and does not dissolve in cold sodium carbonate solution.

When the acid is warmed with aqueous potash for a few minutes and the solution cooled, no precipitate is produced on acidifying (although the original acid is very sparingly soluble in cold water); alcoholic potash also acts readily on the acid, converting it into a very thick colourless syrup, which could not be crystallised. This syrup has an acid reaction, is miscible with water, and dissolves in aqueous sodium carbonate with effervescence, giving a solution which does not reduce potassium permanganate; it seems to be a hydroxy-acid of the composition $C_{10}H_{16}O_5$ (found C=54·2, H=7·4, Calc. C=55 5, H=7·4), but as it was not specially purified the analysis is not decisive.

The pale yellow oil which is obtained along with the bromocamphoric acid is a mixture; when it is warmed with alcoholic potash for some time, and the alcohol evaporated crystals of the original π-dibromocamphor are deposited, and the alkaline solution yields when acidified a crystalline substance which contains nitrogen. This is a *nitrobromocamphor*, $C_{10}H_{14}(NO_2)BrO$ (found C=43·21, H=5·07), but is not identical with the known compound; it separates from a mixture of chloroform and light petroleum in needles melting at 133—134°, and is soluble in aqueous potash and sodium carbonate, but is almost insoluble in water.

25. "*Note on the Action of Diastase on Cold Starch-Paste.*" By Horace T. Brown, F.R.S., and G. Harris Morris, Ph. D.

The authors draw attention to the generalisation which they claim to have established in previous communications, namely, that the products of a starch transformation, or any part of them separated by any method of fractionation, can always be expressed, in the terms of maltose, having an optical activity $[\alpha]_{j3\cdot86}=150°$, and a cupric-reducing power of $\kappa_{3\cdot86}=61$, and of dextrin, having an optical activity of $[\alpha]_{j3\,86}=216°$ and no reducing power; in other words, knowing the cupric-reducing power of any starch product, the optical activity can be predicted with accuracy, and *vice versa.* This fact is quite independent of any consideration of the true nature of the intermediate products between starch and maltose, and has been ignored by certain recent workers.

In a paper by Brown and Heron (*Trans.*, 1879, p. 627) it is mentioned that during the early stages of the action of diastase upon starch-paste in the cold, there is an apparent exception to this rule, the optical activity being *lower* than it should be on the assumption that only maltose and dextrin are present. After standing some hours, or on boiling, this discrepancy disappears, and the optical cupric reducing powers show the same relationship that they do in conversions made at higher temperatures. An observation made by O'Sullivan and Tompson in another direction suggested an explanation of these abnormal results, and in the present paper the authors show that the lower angle of rotation observed during the earlier stages is due to the maltose being liberated in the state of "half rotation," a condition which freshly-prepared solutions of pure maltose always show. When freshly dissolved the optical power of maltose bears the relation to that of a boiled or old solution of about 133° to 150°, and the authors show that this relationship holds good in the case of freshly-prepared products from cold starch-paste.

26. "*On the Magnetic Rotation of some Unsaturated Hydrocarbons.*" By W. H. Perkin, Ph.D., F.R.S.

In this paper it is shown that the magnetic rotations of the olefines do not differ from those of the paraffins to quite such a large extent as do other substances correspondingly unsaturated, the vinyl compounds excepted. In the case of diallyl, which is twice as unsaturated, the increase in the magnetic rotation is, however, proportionally a little larger, being more than twice that of the olefines. A comparison is made of the boiling-points, densities, and specific rotations of the six carbon hydrocarbons, hexane, hexylene, diallyl, and dipropargyl, and it is shown that the differences between dipropargyl and diallyl are not of the same order as of those between hexane and hexylene, being of an opposite kind in the boiling-points and much larger in the other properties. The molecular rotations, however, which involve both density and specific rotation, exhibit greater regularity, the two acetylene linkages influencing the molecular rotation to the same extent as four ethylene linkages. The molecular rotation of isoprene does not differ much from that of diallyl, if the difference of CH_2 in its composition is allowed for.

List of Fellows.

A new List of Officers and Fellows of the Chemical Society being in course of preparation, it is requested that Fellows will send any alteration of Name or Address, without delay, to the Assistant-Secretary, Burlington House, London, W.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, March 4, 1895.

Sir James Crichton Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—His Grace the Duke of Newcastle, Lieut.-Col. W. W. Rawes, R.A., Dr. Marmaduke Prickett, Miss C. E. Bradshaw, Mrs. Alexander Goschen, and Messrs. G. S. Albright, E. G. Betts, R. A. Bray, M. Bulloch, G. Bywaters, G. F. N. Clay, C. S. Dickson, J. J. Elliott, J. Garvie, F. L. Harris, E. G. Harrison, S. C. Hogg, E. Law, G. H. Ogston, B. P. Portal, S. J. Portal, W. T. Shaw, J. H. Skelton, J. J. Walker, W. H. Walker, and A. F. Walter.

The Special Thanks of the Members were returned to Sir William J. Farrer and Mr. John Douglas Fletcher for their donations to the Fund for the Promotion of Experimental Research at Low Temperatures, and to Mr. Hugh Spottiswoode for a portrait of his father, the late Mr. William Spottiswoode.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Dr. Dobbin in the Chair.

The seventh meeting for this Session was held on February 26.

A paper was read by Mr. Alexander Lauder on the "*Fixation of Atmospheric Nitrogen.*"

The paper gave an account of the more important of the different attempts which have been made to utilise the nitrogen of the atmosphere for the preparation of ammonia or potassium cyanide. A description of the process of preparing potassium ferrocyanide from refuse, organic matter, iron, and potassium carbonate was first given, Liebig's theory of the process being briefly discussed. The more important of the various processes proposed for the fixation of atmospheric nitrogen were then considered in historical order.

Attention was first directed to this subject by the discovery of masses of a fused salt at different iron furnaces, which analysis showed to contain a large percentage of potassium cyanide. The source of the nitrogen contained in the potassium cyanide was the subject of active discussion, until accurately conducted laboratory experiments proved that nitrogen is capable of combining with carbon and potassium to form potassium cyanide. Carefully purified nitrogen was passed over a mixture of pure carbon and potassium hydrate, heated in a tube to bright redness, and potassium cyanide was found in the residue. A short account was given of the famous investigation carried out in 1845 by Bunsen and Playfair on a blast furnace at Alfreton which produced potassium cyanide. They came to the conclusion that potassium cyanide was only formed at the temperature at which potassium oxide gives up its oxygen to carbon, and that the conditions favourable to the production of cyanides were a reducing atmosphere and a temperature of the degree already mentioned.

The following was the average composition of the gas drawn from the furnace through a hole made in the front wall about 2 ft. 9 in. above the blast pipes:—

Nitrogen	=58·05	per cent.
Hydrogen	= 3·18	,,
Carbonic oxide ..	=37·43	,,
Cyanogen	= 1·34	,,

After the possibility of direct combination of nitrogen with carbon and potassium had been proved, attempts were immediately made to apply the principle to manufacturing purposes on the large scale. Many patents were taken out for this purpose, but the majority of them were quite unsuccessful. The process of Pessoz and Boissiere,[*] carried on first at Grenelle, near Paris, and latterly at Newcastle-upon-Tyne, was considered in some detail. In this process the atmospheric air was first passed through a coal fire to convert the oxygen into oxides of carbon; the mixed gases next passed through white-hot flues to large cylinders of fire-clay charged with charcoal saturated with potassium hydrate, and which were also kept at a white-heat. The process worked continuously, the cyanised charcoal being drawn off at the bottom, and more alkaline charcoal fed in at the top. The works were continued for three years (1844 to 1847), and were then abandoned after considerable loss. The cause of failure was principally due to the rapid destruction of the retorts by the potash at the high temperature necessary to carry out the reaction.

Other processes, in which baryta was used as the base instead of potassium hydrate, were also considered. The paper concluded with a short discussion of the various conditions which experience has shown to affect the process, *e.g.*, the temperature at which the reaction is carried out, the action of the base which is always present, the most suitable base to use, and the influence of water vapour and of oxygen on the reaction.

NOTICES OF BOOKS.

Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics. By Prof. Walter Nernst, Ph.D. (of the University of Göttingen). Translated by Prof. Charles Skeelo Palmer, Ph.D. (of the University of Colorado). With Twenty-six Woodcuts and Two Appendices. 8vo., pp. 697. London and New York: Macmillan and Co. 1895.

In noticing a work of this kind we have to consider not only the author, but the translator. That Prof. Palmer thoroughly understands and appreciates Prof. Nernst cannot be questioned. But whether the former has always succeeded in making "the sound German speak good English" is sometimes doubtful. Thus whether or no the expression "Waermetönung" was the happiest possible, it is undeniably good German. But "heat-toning," here used as its equivalent, cannot be regarded as good English. Prof. Palmer repeatedly uses "knall-gas" as a translation of the German Knall-gas where we should say "detoning-gas." The misfortune is that any Englishman, except he has been educated in Germany, will pronounce the word "nall-gas." "Schlieren" is a word which cannot be tolerated in an English work; "layers" or "strata" would express the author's meaning with sufficient clearness. As to minor peculiarities in expression and orthography, we cannot expend time and space in their mention.

The work itself is one which deserves the most hearty recommendation. Advanced students will find it an invaluable guide to chemical theory in its present stage of development. After an introduction which will be profitable reading even for the experienced chemist, especially if he understands German, the author undertakes an examination of the universal properties of matter, of the atom and the molecule, of the transformation of matter, and the transformation of energy. These last two books deal very fully with the doctrine of affinity, which, as here pointed out, is originally a biological conception. We must here add that, whilst scarcely satisfied of Prof. Palmer's competence to render a foreign work into English, we have the highest opinion of his merits as a chemical philosopher. The footnotes which he has added greatly enhance the value of the work—*e.g.*, those on pp. 354, 355, 431, &c.

Prof. Nernst, as well as his translator, is far from undervaluing the hypothesis of Avogadro. On the capital but unsolved question whether our reputed elements are anything beyond the present limit of our analytical resources, neither of these authorities pronounces a decided opinion. Prout's hypothesis is definitely rejected (Appendix 1, p. 629), in accordance with the researches of Landolt. It is, however, clear that the near approach to the values which Prout's hypothesis would require is not accounted for.

On p. 296 the author mentions the law discovered by Nietzki, *i.e.*, that the simplest colouring substances are in the greenish-yellow and yellow, and with increasing molecular weight the colour passes into orange, red, violet, blue, and green. This law involves some interesting corollaries which cannot be touched upon in a notice of Prof. Nernst's work. The remark of Schütze is also here quoted, that in analogous elements an increase of atomic weight involves deepening of the colour.

In discussing solid solutions—*i.e.*, the solution of one solid in another—the author refers to the view of Witz, that the process of dyeing consists in the solution of the pigment in the fibre. Thus the dyed fibre does not show the colour of the solid colouring-matter, but of its solutions,—*e.g.*, the cases of magenta, rhodamine, &c. The theory of indicators is explained as according to Prof. Gladstone, Salet, Magnanini, and others.

In controversies Prof. Nernst does not always observe the *leniter in modo.* Thus he refers to Berthelot's "usual offensive style" (p. 585). This is to be regretted.

Appendix II., containing a "synchronistic comparison of the most important chemical journals and allied periodicals," suggests various reflections. We notice, firstly, how far the German journals outnumber those of France, England, and America, taken conjointly. Secondly, we are again impressed with the difficulty of keeping in view the world's entire work in chemistry. Now Memoirs are appearing in Rumanian, Czech, Servian, Polish, and Russian, the task becomes practically impossible. Who can suggest a remedy? The proposal made that whatever is not published in German, French, or English, shall be regarded as unpublished, even if accepted, would not fully meet the difficulty.

It will not be considered a vain repetition if we once again recommend Prof. Nernst's work to students, not as something to be examined in, but to be comprehended and assimilated.

The Specialist's Series. Steel Works Analysis. By J. O. Arnold, F.C.S., Professor of Metallurgy at the Sheffield Technical School, some time Chief Chemist at the Sheffield Steel and Iron Works. Crown 8vo., pp. 350. London: Whittaker and Co., 2, White Hart Street, Paternoster Square. New York: 66, Fifth Avenue. 1895.

This book possesses some very good features, which unfortunately are not in all cases to be found in chemical annuals. The author does not present us with a com-

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[*] See article on "The Fixation of Atmospheric Nitrogen," by Prof. Breneman, Chemical News, 1890.

pilation, but writes from his own experience. Doubtful processes are judiciously left aside, the student or the young expert being thus not bewildered with the choice between methods. He protests against the "appalling elaboration" with which authors on the chemistry of iron and steel discuss the separation of elements possible, but very rare.

A remarkable but not useless feature in this work is the statement of the time whicn each process may be expected to require. We find the remark that, if certain procedures were adopted, "the world would have to wait for its iron." We are here reminded of the utterance of a thinker who represents Nature saying to Man — "Why all this hurry, my little Sir?"

There is a useful list of the materials upon which a steel works' chemist must be prepared to report. Mr. Arnold appends to most of his directions an abstract of the theoretical considerations involved. This course has been adopted because he has found the knowledge of pure chemistry possessed by pupils and junior asistants less than what is commonly and reasonably expected.

At the end of the book we find a list of normal compositions of the substances most commonly encountered by the steel-works' chemist. There is a table of atomic weights, in which we regret to find platinum still figuring higher than gold. There is the *banal* denunciation of English weights, though the decimal system would long ago have been taken into use had it not been encumbered with its present Græco-Latin nomenclature.. Hydrometer scales, in which we have a distinct advantage over our Continental neighbours, are not mentioned.

After considering the apparatus and the manipulations necessary, the author gives in succession instructions for the analysis of the metals and alloys which come under the hands of the steel-works' analyst; of the ores of iron, manganese, chrome, tungsten; of refractory materials, fuels, slags, and boiler-water. Under the last head, of course, many of the determinations most required by the sanitary, the tinctorial, and the zymotechnical chemist, find no mention.

The instructions given for the various processes are of a sound, practical character, and, if carefully and conscientiously followed out, will lead to useful results. Hence, in iron- and steel-works, Mr. Arnold's treatise merits full confidence.

Catalogue of Standard Second-hand and New Books, English and Foreign, on Chemistry and the Allied Sciences, Technology, Physical and Electrical Science, Metallurgy, &c. No. 61. 1884-5. William F. Clay, Chemical, Technical, and Scientific Bookseller, University Book Warehouse, 18, Teviot Place, Edinburgh.

We are afresh led to admire the perseverance and business skill with which Mr. Clay continues to obtain rare and valuable works, on terms which enable him to offer them at remarkably liberal prices. We find on this Catalogue complete sets of, *e.g.*, the Chemical News from the very beginning; of the Cavendish Society's publications, which, though now very scarce, are offered at less than one-half the original price; of Liebig's *Annalen*, of *Dingler's Journal*, of Fresenius's *Journal fur Analyt. Chemie*, the *Reports of the British Association* from 1831 to 1888, the *Philosophical Magazine* from the beginning, the *Proceedings of the Royal Society*, &c. These announcements ought to stimulate the Librarians of Universities, learned Societies, &c., into prompt action.

Rare single works are also not wanting, such as the works of Boyle, the papers of J. Clerk Maxwell, the monographs of the late Thomas Carnelley, of C. Schorlemmer. Curious features are the libraries of the late Prince Lucien Buonaparte, and of that of C. O'Neill.

If, by way of contrast, any one wishes to form a collection of the hand-books, manuals, and manualettes of chemistry, in which the English press has been so marvellously fruitful, the Catalogue before us will supply him with the titles.

We think that Mr. Clay's efforts ought to be thoroughly appreciated by chemists and technologists.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxx., No. 7, February 18, 1895.

Plurality of the Chlorophylls. Remarks on M. Etard's Memoir.—Arm. Gautier.—In 1877 the author established not merely the plurality of the chlorophylls, but their power of crystallising, the total absence of iron and the presence of organic phosphorus and magnesium in the crystals of this substance, which are soluble in carbon disulphide and in ether (see *Comptes Rendus*, cxx., p. 328, and cxix., p. 289).

Agricultural Value of Aluminium Phosphates. Comments on the Memoir of M. Andouard.—Arm. Gautier.—If minervite $(PO_4)_2Al_2,7H_3O$, of bacterial origin, and in general the aluminium phosphates, more or less amorphous, which have had their origin in the decomposition of guanos and other organic matters, and which have derived their alumina from the surrounding rocks, are easily assimilable in the soil, this property cannot be ascribed to the crystalline double calcium and aluminium phosphates of ancient hydro-mineral origin, or to crystalline aluminium phosphates such as gibbsite, wavellite, &c. The phosphoric acid of these minerals, when finely ground, is not more rapidly or more usefully utilised by plants than that of crystalline apatite. My observations and those of M. Andouard apply only to the phosphates which have indirectly originated from the fermentation of nitrogenous matter.

The Determination of Tannic Compounds.—Aimé Girard.—This paper will be inserted *in extenso.*

Remarks on Atomic Weights.—Lecoq de Boisbaudran.—(See p. 116).

Properties of Amorphous Silicon.—M. Vigouroux.—This paper will be inserted in full.

Oxidation of the Tannin of the Cider Apple.—L. Lindet.—We may accept it as an established fact that the oxidation of the tannin of the apple is due to the action of a diastase enclosed in the tissue of the fruit and belonging to the type of the laccases. Further research is required to show whether this is directly due to oxidation, or if it splits up the tannin into molecules more easily oxidised.

Composition and Analysis of Brandies. — . Rocques.—In the analysis of brandies the most definite elements to be recognised are the total amount of volatile substances other than ethylic alcohol, the quantities of ethers and higher alcohols, and the relative proportions of these substance.

Seeds of Moâbi.—H. Lecomte and A. Hébert.—The tree yielding belongs to the family of the *Sagotaceæ*, growing in French Congo. The sap of the bark yields on coagulation a product rich in gutta-percha. The nuts yield from 30 to 35 per cent of a fatty matter. The cake, after the only matter has been dissolved out by benzene, contains 4·05 per cent of nitrogen, and may be valuable as a manure or as cattle food.

Revue Universelle des Mines et de la Metallurgie.
Vol. xxix., No. 1.

New Researches on Chromium.—H. Moissan.—Already inserted.

Atomic Weights of Nickel and Cobalt.—Prof. Winkler (*Zeitsch. fur Anorganische Chemie*).—Already noticed.

MISCELLANEOUS.

Hackney Vestry.—Appointment of Public Analyst. —In an advertisement which appeared in our issue of Feb. 8th the date for receiving applications for this appointment was given as the 18th inst., and for making the appointment the 28th inst. The latter date should have been altered in the next issue to the 27th; but we regret that, instead of this, the date for receiving applications was, by an unfortunate error, altered to the 27th inst.

Certain Derivatives of Phenolphthalein.—A. Hallre and A. Guyot.—Both the procedures employed for the preparation of diethylphthalein yielded one and the same derivative, which does not seem to possess the quinonic grouping. On varying the conditions of the experiment in all possible manners, they never obtained oxime with this ether, nor with the diphenylphthalide of the residue. —*Comptes Rendus*, cxx., No. 6.

Method of Formation of Cyanamide.—Ch. Moureu. —Urea and cyanamide differ from each other by the elements of water. This reaction is fundamentally that which connects the amides to the ammoniacal salts, only in the present case, the amide being cyanamide, the ammoniacal salt, corresponding to ammonium cyanate, is replaced by carbamide or urea. In the same manner as cyanamide has been hydrated and transformed into urea, urea can lose 1 mol. of water and be converted into cyanamide.—*Bull. Soc. Chim. de Paris*, No. 22, 1894.

Researches on Mercuric Picrate.—Raoul Varet.—If the author's thermic values are compared with those obtained by Berthelot for mercury acetate, chloride, and cyanide, other soluble salts of the same metal, we find that the picrate ranks with the acetate, the neutralisation heat of which by HgO liberates +6·0 cal. It will be remarked also that picric acid, in contradistinction to hydrocyanic acid, with potassa displaces it in the solution itself, and without precipitation, liberating +16·7 cal., which answers to a thermic preponderance of the former acid towards this base. On the contrary, with mercury oxide hydrocyanic acid liberates 12·2 cal. for each mol. of acid, which answers to the thermic inversion of the two acids in presence of mercury oxide.—*Bull. Soc. Chim. de Paris*, No. 22, 1894.

MEETINGS FOR THE WEEK.

Monday, 11th.—Medical, 8.30.
Tuesday, 12th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
—— Medical and Chirurgical, 8.30.
—— Photographic, 8.
—— Institute of Civil Engineers, 8.
Wednesday, 13th.—Society of Arts, 8. "The Meat Supply of the United Kingdom," by E. Montague Nelson.
—— Pharmaceutical, 8.30.
Thursday, 14th.—Royal, 4 30.
—— Mathematical, 8.
—— Institute of Electrical Engineers, 8.
—— Society of Arts, 4.30. "Art Tuition," by Prof. Hubert Herkomer, R.A.
Friday, 15th.—Royal Institution, 9. "The Rarer Metals and their Alloys," by Prof. Roberts-Austen, C.B., F.R.S.
—— Quekett Club, 8.
Saturday, 16th.—Royal Institution, 3. "Waves and Vibrations," by Lord Rayleigh, F.R.S.

THE CHEMICAL NEWS

Vol. LXXI. No. 1842.

ISOMERIC NAPHTHALENE DERIVATIVES.*

The Conversion of Sulphochlorides into the Corresponding Chloro-derivatives.

In the case of naphthalene derivatives no interaction is of greater practical importance than that which occurs when sulphochlorides are heated with phosphorus pentachloride, whereby they are converted into chloro-derivatives.

At one time it was argued that reliance could not be placed on this interaction as a means of determining constitution; but of late years no such objection has been raised. and the idea that isomeric change may attend the displacement of the sulphonic radicle by chlorine appears to have been abandoned. The results obtained, especially by Cleve and Dr. Wynne and the writer, are so uniformly consistent, *inter se*, that, bearing in mind the extent of the field covered, there is no longer room for doubt. Observations made during the past year are of interest as throwing light on the natnre of the interaction.

There have long been instances on record of the conversion of sulphochlorides into corresponding chloro-derivatives and sulphur dioxide ($RSO_2Cl = RCl + SO_2$) by mere distillation.

The successful use recently made of this method in the writer's laboratory, in preparing chloro- and bromo-derivatives of camphor, by Dr. Kipping and Mr. Pope, has led him and Dr. Wynne to systematically study the behaviour of naphthalene sulphochlorides, which they had long known underwent decomposition, evolving sulphur dioxide, when heated. The conclusion arrived at is that, in all probability, phosphorus pentachloride acts merely by facilitating the resolution of the sulphochloride into sulphur dioxide and the chloro-derivative by attacking the former and converting it into thionyl chloride; and that, in fact, the chlorine in the chloro-derivative is not improbably the original chlorine of the sulphochloride and not chlorine derived from the pentachloride. In most cases the amount of chloro-derivative produced by directly distilling the sulphochloride is inferior to that obtained by means of pentachloride, as the decomposition is facilitated by the chloride, and therefore takes place at a lower temperature in its presence. There is always more or less of a resinoid condensation product formed on distilling the sulphochloride, but the amount is in some cases very small, while in others practically nothing else is obtained. On the other hand, in the case of compounds which are very readily chlorinated, the method permits of the production of chloro-derivatives corresponding to the sulphochlorides, which are almost unprocurable from them by the ordinary method. For example 1 : 1'-chloronaphthalenesulphonic chloride yields a very large proportion of 1 : 1' dichloronaphthalene when distilled, although when heated with phosphorus pentachloride it is almost entirely converted into 1 : 4 : 1' trichloronaphthalene. The α-sulphochlorides appear all to decompose more readily, and to yield a larger proportion of chloro-derivatives than do the β-sulphochlorides. It may be added that, taking into account the readiness with which change occurs during sulphonation, the non-occurrence of isomeric change on distilling sulphochlorides is probably significant.

Bromo-derivatives of Naphthalene.

The conversion of naphthalene sulphobromides into corresponding bromonaphthalenes by means of phosphorus pentabromide is attended with great difficulty, as the bromide frequently acts almost exclusively as a brominating agent, owing to the readiness with which it is resolved into the terbromide and bromine. Far better results are obtained in many cases by merely distilling the sulphobromide, although the formation of higher bromo-derivatives is not entirely avoided. During the year Mr. Jenks and the writer have made considerable progress in completing the series of bromonaphthalenes (di- and tri-derivatives), and in determining the nature of the sulphonic acids prepared from the dibromonaphthalenes by Mr. Rossiter and the writer.

One result of which mention may be made relates to the tribromonaphthalene obtained by Jolin by distilling nitro-1 : 4-dibromonaphthalene with phosphorus pentabromide, which has always been represented as the 1 : 4 : 1-derivative, apparently because it is supposed that, as a rule, α nitro-compounds are formed on nitrating naphthalene derivatives. Judging from the low melting-point of the tribromonaphthalene in question, it is improbable that it is a tri-α-derivative, as such a tribromonaphthalene should melt at a much higher temperature. The accuracy of this conclusion is established by the observation that 1 : 4-dibromonaphthalene hetero-β-sulphonic bromide is converted by distillation into a tribromonaphthalene which is undoubtedly identical with that prepared from nitro-1 : 4-dibromonaphthalene.

Attempts to devise a satisfactory method of preparing 1 : 1'-dibromo-naphrhalene had been made by Mr. Jenks and the writer prior to Meldola's discovery of this modification, and, as these have been continued to a successful issue, reference may be made to the subject. The first method devised involved brominating the acetyl-derivative of Guareschi's 1 : 4'-bromonaphthylamine, prepared by brominating nitronaphthalene, &c.; this readily affords what appears to be a 1 : 1'-dibromacetnaphthalide, but the greatest difficulty has been experienced in hydrolysing this compound.

A second method consists in nitrating 1 : 4-bromonaphthalene sulphochloride. A 1 : 1'-nitrobromosulphochloride is readily obtained, but, although the chief product, it is by no means the only one.

A third and far simpier method consists in heating 1 : 4-bromonaphthalene sulphochloride with bromine, and subsequently hydrolysing the 1 : 1 dibromosulphochloride, which is almost the exclusive product when the operation is properly carried out.

Although it is known that naphthalene hetero-β-sulphonic acid is very readily converted into 1 : 4-dibromonaphthalene hetero-β-sulphonic acid, the order in which the bromine atoms enter has not been determined; and it is, in fact, difficult to arrest the action at an intermediate stage, the tendency to form the dibromo-derivative being very great. Mr. Stallard, however, having kindly placed a quantity of monobrominated β-sulphonate at the writer's disposal, it has been ascertained that it is an α_1-bromo-β_3'-derivative. By heating naphthalene-β-sulphochloride with a molecular proportion of bromine, a very satisfactory amount of 1 : 3'-bromosulphochloride is readily obtained. The "repellent" influence of an acid radicle is clearly brought out by these results, as β-bromonaphthalene yields 1 : 2'-dibromonaphthalene when brominated.

It is well known that there is often great difficulty, especially in the case of α naphthol and α-naphthylamine, in obtaining satisfactory yields of bromo-derivatives, a considerable amount of by-product being formed, the nature of which has not been understood hitherto. Some light has been thrown on the nature of these products by observations made by Mr. Jenks and the writer.

Following the directions given by Cosiner and by Claus and Phillipson, monobrom-β-acetnaphthalide was prepared by mixing bromine with β-acetnaphthalide dis-

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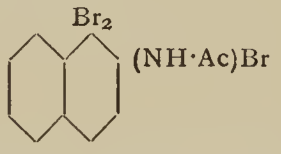
* Eighth Report of the Committee, consisting of Professor W. A. Tilden and Professor H. E. Armstrong (drawn up by Professor Armstrong). Extract from "The British Association for the Advancement of Science," page 268.

solved in acetic acid. Although the conditions were greatly varied, the amounts of pure product obtained were in all cases very unsatisfactory, rarely exceeding 25 per cent. The main product was a crystalline substance, more soluble in alcohol than monobromo-β-acetnaphthalide, but almost insoluble in acetic acid, ethylic acetate, chloroform, xylene, and water. When digested with a weak solution of caustic soda, this substance is converted into monobromo-β-acetnaphthalide, and the same effect is produced by digesting it with a solution of either sulphurous acid or potassium iodide. It appears to be probable that this substance contains the elements of a molecule of bromo-β-acetnaphthalide and a molecule of bromine; such a compound would contain 56·6 per cent of bromine. The highest amount found was 52 per cent, but as the substance undergoes decomposition when recrystallised from alcohol, it cannot be obtained pure. It is not produced by brominating bromo-β-acetnaphthalide, and therefore is probably formed together with it, being perhaps an addition compound, such as is represented by the formula—



By digesting the crude product of the action of a single molecular proportion of bromine on one of β-acetnaphthalide with a weak solution of caustic soda, and then recrystallising from spirit, as much as 75 per cent of the theoretical yield of bromo-β-acetnaphthalide can be obtained.

Rule Expressive of the Formation of Sulphonic Acids.

Dressel and Kothe, in a recent most interesting paper (*Berichte*, 1894, 27, 1193—1210), have taken exception to the "rule" suggested by Dr. Wynne and the writer, referred to in previous reports, that there is an "invincible objection" on the part of two sulphonic groups to *remain* in either contiguous or para- or peri-positions; they have described a tri- and a tetra-sulphonic acid, each containing two sulphonic radicles in contiguous ββ-positions. We shall have occasion to discuss their results when the investigation of the changes attending sulphonation—the most difficult and complex chapter of the subject—is somewhat further advanced. It is only necessary to say that the "rule" was merely an expression of the results up to that time obtained, and was never intended as a final statement.

ON A NEW ELEMENT EXTRACTED FROM RED FRENCH BAUXITE.

(Preliminary Note).

By Dr. R. S. BAYER.

The products of concentration derived from any mineral industry are always an interesting subject of research. We may find in them the presence of substances very different from those which form the principal object of the treatment, and sometimes we may detect novel elements which are still wanting in the periodic series of Mendeleeff.

Such are the dusts of blast-furnaces, the mother-liquors, the substances which remain in the cycle of a manufacture, and we owe the knowledge of a certain number of elements to these processes of concentration. We may mention as instances the discoveries of iodine, bromine, cæsium, rubidium, selenium, thallium, vanadium, &c.

Eight years ago I had occasion to occupy myself with a considerable quantity of a concentration product obtained from the treatment of the red bauxite of the Var. I propose to give here the results, still incomplete, of my researches which my industrial occupation have not given me leisure to complete. I will first say a few words on the origin of the product. In the old procedure for the preparation of pure alumina, the bauxite, finely powdered, was calcined with sodium carbonate or caustic soda in a reverberatory until the formation of sodium aluminate. The mass was dissolved in water, and in the filtered solution of aluminate the aluminium hydroxide was precipitated with carbonic acid. The solution containing the sodium carbonate regenerated was evaporated and served for the treatment of a further quantity of bauxite.

In the calcination of the bauxite there is formed, besides, sodium sulphate on account of the sulphur contained in the coal. After a certain time the quantity of sulphate was such that the mass taken from the furnace was very hard and difficult to dissolve. On this account it became necessary to withdraw from the circulation these lyes of alumina in order to purify them after the precipitation of the alumina with carbonic acid.

This purification was effected by means of successive crystallisations; the mother-liquors were concentrated until they no longer deposited crystals. The last mother-liquors had a specific gravity of 42° B. They were in quantity about 1000 litres, an oily liquid of a deep yellowish brown, and contained all the acids of the metals forming with sodium salts soluble in water. They contained also a small quantity of organic substances.

These lyes were the crude material from which I set out in my researches.

If we further add to these lyes a little caustic soda, we obtain fine yellowish octahedra, which I recognised as the well-known compound of sodium orthovanadate with sodium fluoride, answering to the formula—

$$2Na_3VO_4\cdot NaFl+19H_2O.$$

The traces of fluorine contained in the bauxite, and which cannot be manifested by any other process, had accumulated in the soda and given rise to this compound.

More simply, and without any loss of the rare matters, we obtain the same liquids by following my new patent process for the treatment of bauxite. In this process the pulverised bauxite is treated with alkaline liquors, either caustic soda or sodium aluminate decomposed and concentrated up to 45° B.

The alumina alone dissolves, and the ferric oxide, with all other accessory elements, remains in the red residue. If we ignite this residue with about 3 per cent of caustic lime for two to three hours in the oxidising flame of a reverberator, we may extract with water all the sodium salts formed, and thus obtain a yellow solution containing all the above-mentioned elements. There always remains alumina in the state of sodium aluminate; it is preferably precipitated by carbonic acid, and after filtration and washing, the solution is evaporated to crystallise all its salts, until we obtain a liquid of the specific gravity 40° to 42° B.

The qualitative analysis of these mother-liquors showed as the main constituent sodium sulphate and carbonate with notable quantities of chromic and vanadic acids; then molybdic acid and traces of silica, alumina, arsenic acid, phosphoric and tungstic acids, magnesia, lime, &c.

I first precipitated from these solutions the vanadium. For this purpose I added to the liquid a fourth of its volume of water, and after heating to 40° to 50° I added ammonium chloride to saturation. I added further a small excess of ammonium chloride and digested for twenty-four hours, stirring from time to time. At the expiry of this time the chief part of the vanadium was deposited as ammonium vanadate.

On evaporating the liquid and adding a little ammonia, nearly all the rest of the vanadium was precipitated. But as other salts crystallised at the same time, it was necessary to treat the precipitates several times with a little cold water, which dissolves the salts and leaves the ammonium vanadate undissolved.

Still there remains a small quantity of this substance which cannot be removed thus, and of which hereafter.

The liquors thus freed as far as possible from vanadium are boiled with the addition of a little caustic soda, and a current of hydrogen sulphide is introduced until a small specimen filtered gives no precipitate when heated with a little ammonium sulphide. We thus precipitate all the chromium as hydroxide, but the precipitate carries down small quantities of vanadium, phosphoric and arsenic acids, &c. With the greatest precautions it is impossible to precipitate in this manner absolutely pure chrome, when there are other elements in the solution. An exact analysis of researches on this precipitate has yet to be made.

The chromium hydroxide precipitated filters very well; it has not the gelatinous aspect which this substance affects.

We have next to treat the filtrates from the chromium hydroxide. If we proceed as mentioned above the metallic acids are transformed into sulphides only to a small extent. To effect this transformation it is necessary to pass into the solution a current of hydrogen sulphide to complete saturation. If needful we filter again and add to the filtrate hydrochloric acid until the reaction is strongly acid. We stir strongly, and heat when the precipitate agglomerates and can be easily washed by decantation.

The remaining liquids contain nothing remarkable, and may be rejected.

The precipitate, which is dark brown, has especially attracted my attention. In it we have to search for only those elements which form sulphides soluble in the alkaline sulphides. The well-known elements of this class are antimony, arsenic, molybdenum, selenium, tellurium, vanadium, tungsten, and tin. The precious metals belong also to this group, but if there were any they would be left with the iron in the insoluble residues from the attack of the bauxite. Researches carried out have not given any indication of the presence of these metals.

Researches on the Precipitate of the Sulphides.—After desiccation this precipitate appears of an earthy brown; it burns if heated in the air, giving off sulphurous acid and leaving a light brown powder.

If treated with strong nitric acid it is heated to ignition. If thus treated until entirely oxidised it leaves a small quantity of a lemon-yellow precipitate in a deep brown solution. This yellow precipitate is found in great part to be a compound of molybdic and arsenic acids. It is easily soluble in ammonia, and gives with magnesium salts in presence of ammonium salts a greyish white crystalline deposit, and in the liquid we can easily detect molybdenum by its known reactions. But at the same time we may recognise reactions and colourations which lead us to suppose that other researches are necessary.

The brown acid solution still contains vanadium, molybdenum, and also traces of selenium.

The last-mentioned substance is derived without doubt from the pyritic coal used in the calcination, and which contains traces of selenium. It was not possible to show the presence of antimony, tellurium, and tin, but traces of tungsten were found in the yellow precipitate formed by nitric acid.

The crude sulphides precipitated by hydrochloric acid containing always organic matters and sulphur I first ignited after having satisfied myself that none of the other substances were volatilised and that no loss was occasioned. On complete ignition the sulphur, arsenic, and selenium were volatilised almost entirely. The residue of this ignition was then treated with ammonia until nothing further was dissolved, and the slight residue was thrown away as containing nothing remarkable. The filtered ammoniacal liquids were concentrated with the addition of a little ammonia.

Being convinced that ammonium nitrate precipitates ammonium vanadiate well, I added it until the liquid is saturated. We thus separate all the vanadium in the state of ammonium vanadate, which is then removed by filtration.

The filtrate on further concentration deposits several kinds of crystals of an olive-brown and of ammonium molybdate. They may be easily separated, because the former are much less soluble in water than in the latter.

These small crystals contain the new element which I have detected, but they still contain molybdenum. This latter substance may be separated by treating the solution of these crystals in water acidulated with hydrochloric acid with hydrogen sulphide at a temperature of near 70°; the new element is not precipitated by hydrogen snlphide in acid liquids.

The filtrate is then evaporated in the air; at the commencement it is of a violet-blue, but it becomes of a lemon-yellow from the absorption of oxygen.

The small quantity of molybdenum not precipitated is converted into acid. In this state it is precipitated by hydrogen sulphide, and the precipitations and re-oxidations must be repeated until the last precipitate is of a pure white, *i.e.*, free from sulphur.

By this treatment we finally obtain a brown precipitate of molybdenum sulphide and a violet liquid like red wine diluted with water. I satisfied myself repeatedly that the molybdenum sulphide does not carry down any trace of the new element.

The violet liquid, exempt at last from vanadium and molybdenum, contains the new element in the lowest stage of oxidation, whilst the yellow liquid obtained by evaporation in air contains it in the highest state of oxidation.

In this state the substance plays the part of an acid, corresponding probably to the formula R_2O_3, and gives characteristic compounds with the various bases.

The acid itself is soluble in water; on evaporation it deposits a yellow crystalline precipitate, which at a temperature of bright redness melts with difficulty to a brownish yellow mass.

Ammonia converts the acid into a crystalline powder of an olive colour, which dissolves readily in hot water and crystallises in small cubes from the cooling solution. The solution has an olive-green colour, and is precipitated by concentrated ammonia.

I recall here the communication which I made to the Chemical Society of Paris at its meeting of May 28, 1894, in which I gave briefly the results obtained and the reactions of my novel element up to this day.

Hydrogen Sulphide.—I have already spoken of the behaviour of this reagent with acid liquids. I add further that the liquids reduced by hydrogen sulphide, concentrated in a current of hydrogen in the absence of any oxidising agent, give with ammonia a bulky precipitate; this precipitate is of a deep violet-brown, and soon becomes crystalline. The supernatant liquid has always a light violet colour, because the precipitation is not complete.

The solutions of caustic soda and sodium carbonate precipitate these liquids also incompletely; but the precipitates re-dissolve in an excess of the precipitant.

Barium and calcium chlorides, &c., give in concentrated solutions violet-grey precipitates.

Ammonium Sulphide and the other alkaline sulphides give with the yellow liquid solutions of an intense cherry-red. There is formed a sulphur salt from which acids precipitate a sulphide of a rust colour. But with the utmost precautions we cannot render the precipitation complete; the supernatant liquid remains of a rust colour.

Barium Chloride gives in the ammoniacal solutions of the salts a greenish yellow precipitate easily soluble in acids and forming a light yellow liquid.

Mercurous Nitrate gives a straw-coloured precipitate soluble in nitric acid; warty crystals are obtained from the solution.

Silver Nitrate gives a green precipitate. This precipitate is soluble in nitric acid and also in ammonia. If the solution in the latter reagent is effected in heat, the silver salt crystallises out on cooling.

Magnesium Chloride in an ammoniacal solution with the addition of ammonium chloride gives at first no precipitate; after some time, and especially if the sides of the glass are rubbed, there is formed a characteristic green precipitate analogous to that of phosphoric acid. Slow precipitation yields crystals large enough to be recognised with the lens. The separation is almost complete, and the liquid, which is green at first, becomes quite decolourised. Yet barium chloride still produces a slight greyish precipitate.

Molybdic Liquor gives in solutions acidified with nitric acid a yellowish white precipitate which deposits with difficulty. The precipitation is very incomplete, and the liquid remains of a strong yellow colour.

Hydrogen Peroxide gives no change of colour either in the acid or the alkaline solutions. It is well known that this reagent gives a very decided reaction with vanadium.

Potassium Ferrocyanide.—This reagent, very sensitive for vanadium and molybdenum, occasions no change in the solutions.

The chlorides of the new element seem to be volatile. From a solution which contained much ammonium chloride to separate the vanadium, I attempted to expel the ammonium salts by volatilisation. In this operation I observed notable losses of the rare element in the state of chloride. There was formed a yellow sublimate, soluble in water, and the vapours escaping from the crucible formed, with the watery vapour from the flame gases, a faint violet-brown light between the crucible and its cover.

I regret to say that it has not yet been practicable to collect enough of the substance for quantitative determinations. From 1 million kilos. of bauxite I have been able to obtain only about 2 grms. of the ammonium salt. Nevertheless I believe that there are serious reasons to infer the discovery of a new element. The spectroscopic examination has shown very characteristic rays in the green, the blue, and the violet.

From want of time and of sufficient apparatus these rays have not yet been determined with sufficient precision. I hope that after some time I shall be able to prepare matter sufficient for a determination of the atomic weight, to affect analysis of the characteristic salts and the determinations which are still wanting.

On the Red Ferruginous Residue from the Treatment of Bauxite.—After having extracted all the acids by calcination with lime, and thoroughly washed the residue, the latter is not yet pure ferric oxide. It still contains numerous elements in addition to iron and aluminium. I have ascertained the presence of silicon, calcium, magnesium, manganese, phosphorus, and titanium. The last-named element is present in combination with sodium, and as $NaHTiO_3$, and may be extracted almost entirely with a little silica, which is found in a double combination with soda and alumina—

$$(Al_2Na_2.Si_3O_{10}+9H_2O).$$

It is sufficient to treat it with weak sulphuric acid containing 8 to 10 per cent of H_2SO_4. We digest for three or four hours at a temperature not exceeding 50°, stirring from time to time.

The filtrate is then boiled with the addition of a little sodium bisulphite, and, after dilution, with an equal volume of water. It is advisable to boil it for 1½ to 2 hours in a wooden trough lined with lead, by direct steam. The titanic acid is deposited almost pure, and it may be purified by known methods.

There are still doubtless other elements in this residue, but the difficulty has been to separate them from the iron and to treat considerable masses of these residues.—*Bull. de la Soc. Chim. de Paris*, Series 3, xi. and xii., No. 24.

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.*

By AMOS PEASLEE BROWN.

(Continued from p. 121).

A. A. Julien (*Ann. N. Y. Acad. Sci.*, iv., pp. 154, 155) has shown that different samples of pyrite show a difference in their reaction with bromine vapour. His experiments consisted in exposing finely ground pyrite to the action of bromine vapour at the temperature of the air for twelve hours. The residue was extracted with dilute H_2SO_4, which removed the iron rendered soluble (bromide), and the iron was then determined in this solution. The percentage of iron that had dissolved varied from 2·43 to 15·20 per cent, although all samples tested are described as pyrite. He also tried the action of bromine in aqueous solution, but the reaction was too rapid to give any comparative results.

Much more important are the results obtained in the oxidation of these minerals by the electric current as conducted by Prof. Edgar F. Smith (*Journ. Franklin Inst.*, cxxx., pp. 152—154), and it was the remarkable results that were then obtained that induced me to continue the study of the comparative reactions of these two minerals. Smith found that a current which would completely oxidise the sulphur in marcasite in a given time would oxidise less than half of the sulphur in pyrite in the same time. This remaining sulphur was held very tenaciously, though the mineral was subjected to more powerful currents and longer continued action than in the case of marcasite or pyrrhotite. Finally, by adding an equal quantity of CuO, and using a more powerful current, all of the contained sulphur was oxidised. Previous to the addition of CuO but 21 or 22 per cent of the sulphur was oxidised. In concluding the article above referred to, the author questions whether the crystalline form alone can make this difference in the action of the two minerals when under the influence of the current.

The two samples of pyrite and marcasite that I selected for the following study were chosen after considerable examination of material as being typical of the two forms of FeS_2. The pyrite was from the hematite mines of Elba. It is exceptionally pure, and free from decomposition or tarnish. Before deciding on it finally pieces were ground and polished, and then examined under the microscope with powers ranging from 50 to 200 diameters, in order to see if it contained any enclosures or varied in texture. It was perfectly homogeneous and showed no enclosures. It took a high polish. The crystals showed the combination of octahedron and pentagonal dodecahedron $\mathrm{O}+\frac{{}^{2}\mathrm{O}^{\infty}}{2}$. Some of the crystals were coated in places with scales of hematite, but this was all carefully removed in breaking up material for experiment. The colour was bright brass-yellow; the specific gravity was determined as 5·179. The marcasite was from the zinc mines of the Subcarboniferous of Joplin, Jasper County, Mo., finely crystallised in polysynthetic twinnings. The freshly-broken crystals show a greenish yellow colour, almost white, but they tarnish readily with bluish or brownish colours. No gangue was present, everything dissolving completely in nitric acid. This marcasite was examined with the microscope in the same way as the pyrite; it did not take such a high polish on account of a fibrous structure, but no foreign matter was found with a power of 200 diameters. Its colour was uniform throughout, showing that no pyrite was present. The specific gravity as determined was 4·844.

In preparing material for experiment only sufficient was ground for immediate use to avoid any chance of oxidation of the ground material; the stock samples of the two minerals broken to nut size were kept in stoppered

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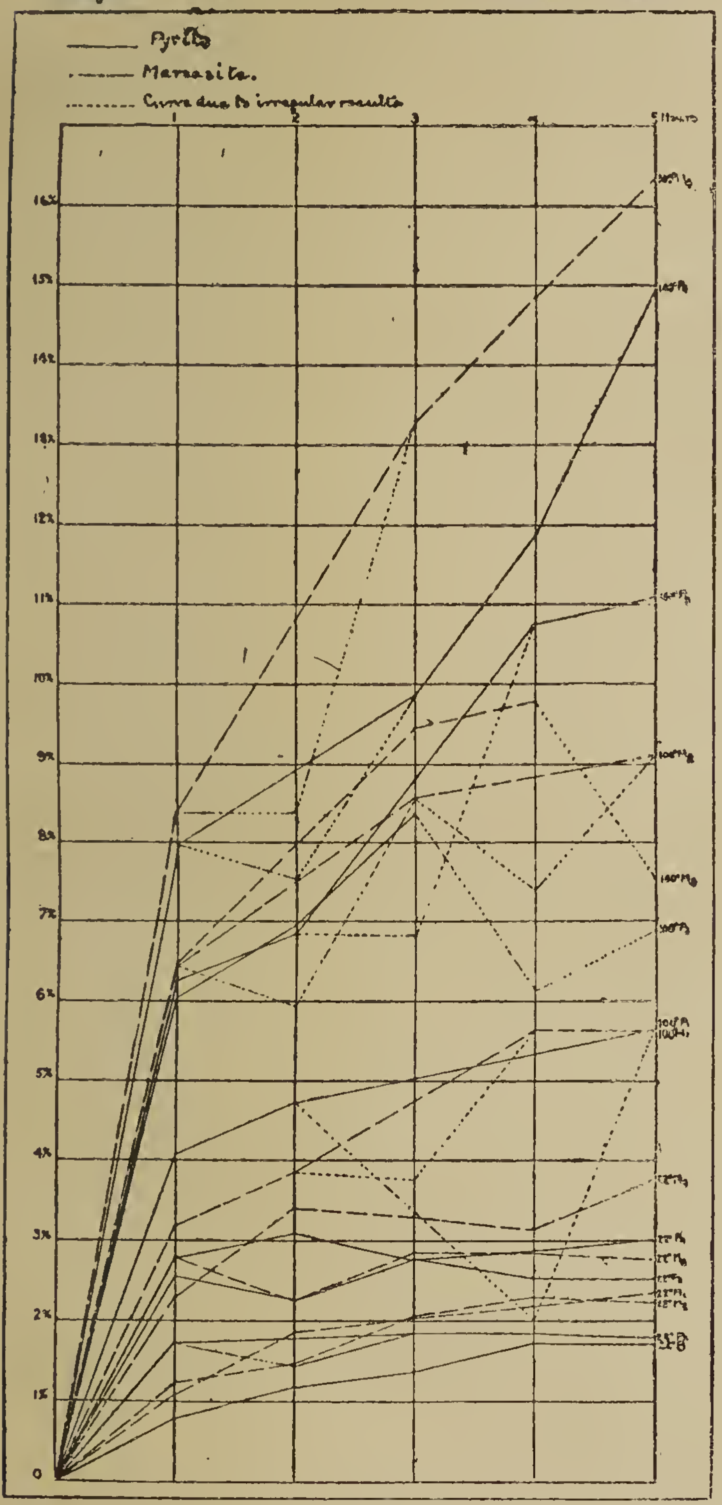
* Read before the American Philosophical Society, May 18, 1894. —From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

bottles. The grinding of material was continued as long as grit appeared, but no bolting was resorted to.

As the experiments of Prof. Smith on oxidation by the electric current showed such remarkable results, my first experiments were on oxidation. As an oxidising agent potassium permanganate ($KMnO_4$) was used, several strengths of which were tried for varying intervals of time with each mineral, and the amount of sulphur oxidised to sulphuric acid determined in the liquid by precipitating as barium sulphate. The object was to secure a complete series of results which would show the comparative rates of oxidation of the sulphur in the two minerals. Neutral aqueous solutions of the potassium permanganate were used, and the strengths of solution employed were $\frac{1}{100}$ normal, 1 per cent, 3 per cent, and 5 per cent; the periods of oxidation extending over one, two, three, four, and five hours, and the entire series being performed at ordinary temperatures and at 100°. As duplicate determinations were made in the majority of cases (I made about 130 determinations of sulphur as barium sulphate), this work consumed a large amount of time, and prevented as full a study of some other reactions of the two minerals as had been originally intended. The following are the detailed descriptions of my processes and results:—

Proceedings Amer. Philos. Soc. Vol. XXXIII, No. 145. Plate XVII.



Action of $\frac{1}{100}$ Normal Potassium Permanganate Solution at Ordinary Temperature.

These oxidations were performed as follows:—Two-tenths of a grm. of the finely powdered mineral was placed in a stoppered bottle of about 100 c.c. capacity, then 50 c.c. of the permanganate solution added, and the contents of the bottle violently shaken to break up lumps. This shaking was repeated about every fifteen minutes while the oxidation lasted. The temperature of the room was at the same time recorded. As stated, the oxidation was continued for one, two, three, four, and five hours with each mineral, making at least ten experiments necessary for each strength of solution. After the solution had acted for the required time it was rapidly filtered through asbestos with aid of the filter pump, the filtrate transferred to a beaker, 20 c.c. of concentrated hydrochloric acid added, and the whole heated until all manganese was reduced to manganous chloride. If not too acid the solution was then diluted to about 300 c.c., and the sulphuric acid precipitated as barium sulphate. When very acid excess of hydrochloric acid was removed by evaporation or by adding ammonia, the ammonium chloride seeming to facilitate the precipitation. The precipitate was washed with hot water and then weighed. All precipitations were made at boiling temperature and digested hot for at least two hours, and then cold for at least twelve hours more before filtering. The filtrates from most of the cold tests were reduced with metallic zinc and titrated with permanganate, but no iron was found in the solution.

Proceedings Amer. Philos. Soc. Vol. XXXIII, No. 145. Plate XVIII.

The two minerals did not present the same appearance when acted on by the oxidant. Pyrite retained its colour and seemed as pulverulent as when the permanganate was added, but marcasite immediately on the addition of the reagent became coated with manganese dioxide, took on a brownish colour, and showed a tendency to cake together and stick to the sides of the bottle, so that it was with difficulty dislodged. This tendency of the marcasite was more marked with stronger solutions of the permanganate, and was doubtless the cause of much of the irregularity that will be noticed in the results. The reason for this difference in action of the reagent on the two minerals will be discussed later on.

The percentages of sulphur oxidised in the two minerals by this method are shown in the following Table, where all results that were obtained are recorded. The figures show the percentages of sulphur oxidised, calculated on the basis of FeS_2 equal to 100 per cent. It will be noted that the four-hour oxidation of marcasite shows a result that is less than the two-hour. This was due to caking of the mineral against the walls of the bottle, which prevented much of it from coming in contact with the solution. On the whole, this series was about the most satisfactory of the cold experiments with $KMnO_4$, the action of this dilute solution being less rapid, and hence more even than that of the more concentrated solutions; naturally the action ceases with a certain dilution, and hence the four- and five-hour oxidations of pyrite are about equal.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a $\frac{1}{100}$ N. Solution of $KMnO_4$ at 22°.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with $\frac{1}{100}$ N. solution $KMnO_4$ ..	0·78	1·17	1·38	1·74	1·72
Marcasite with $\frac{1}{100}$ N. solution $KMnO_4$ ..	1·07	1·86	2·04	(1·25)	2·38

The curves formed by plotting these results on rectangular co-ordinates are shown in Pls. xvii. and xviii. They are marked 22° M_I for the marcasite, and 22° P_I for the pyrite.

Action of 1 per cent Potassium Permanganate Solution at Ordinary Temperature.

This and also the two following series were performed as described under $\frac{1}{100}$ normal solution above. At least two experiments were tried with each mineral in this and the two following cold oxidations, and whenever a result was notably higher or lower than its duplicate a third or fourth was tried. The tendency of the marcasite to cake, noted in the previous series, became still more marked here, and is doubtless the cause of one of the four-hour oxidations (marked by parenthesis) being notably lower than the three-hour. Such a result is obviously incorrect. On the other hand, the result in the three-hour column which is placed in parenthesis is the highest obtained. This experiment was made at the same time as the one showing 1·93 per cent, but the room was very warm (25°), which may in part account for this high result. It will be noticed that the oxidation of the pyrite seems to stop at the three-hour trial, those following showing no appreciable increase. This is well seen in the graphic representation of these oxidations (Pls. xvii. and xviii.).

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 1 per cent Solution of $KMnO_4$ at 22°.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with 1 per cent solution $KMnO_4$ cold	1·72	1·38	1·85	1·79	1·70
	1·71	1·47	1·87	1·90	1·89
Marcasite with 1 per cent solution $KMnO_4$ cold ..	1·16	1·29	1·93	1·95	2·01
	1·28	1·13	2·19	(1·56)	2·15
			(3·92)	2·69	2·55

(To be continued).

ON THE ESTIMATION OF SULPHUR IN PYRITES.*

By G. LUNGE.

Under the above title, Mr. T. S. Gladding (*Journ. Am. Chem. Soc.*, June, 1894; Chem. News, lxx., p. 181) has published several modifications of the wet assay of pyrites which call for some comment on my part, since these modifications purport to be improvements on my method, contained in the "Alkali-Makers' Handbook," and extensively employed in all countries.

Some of Gladding's modifications are of a less important character, and these can be passed in review very briefly. He does not, like myself, test the sample with its natural moisture, estimating the latter in a special sample, but he dries the whole sample and weighs it out in that state. He employs a whole grm. of pyrites, I only half a grm.: and I do so purposely, because the washing of the precipitates is much easier, and consequently the results are more reliable with the smaller than with the larger quantity. In lieu of the mixture of acids employed by me (3 volumes of nitric acid of sp. gr. 1·42, and 1 vol. of fuming hydrochloric acid), Gladding decomposes the pyrites with a solution of bromine and nitric acid. The prescription for that solution is not correct as printed, for 75 grms. of potassium bromide cannot possibly be dissolved in 50 grms. of cold water, or anything like that quantity; but this may be a clerical error, which does not matter very much, as ultimately the solution is diluted to 500 c.c. I will say at once that the bromine solution works well, but no better than the acid mixture according to my prescription.

A more important modification is the following:—It is well known that in the presence of iron the precipitate formed by barium chloride in a solution of sulphates cannot be freed from iron, and that the results of the estimation of sulphur in this case are too low; in my publication of 1879 (*Zeitschr. Anal. Chem.*, xix., 419) I found on the average 0·19 per cent too little sulphur, unless the iron had been previously removed from the solution. Fresenius has also worked on this subject, and Jannasch and Richards, in 1889, completely elucidated it by proving that a double sulphate of barium and iron was formed in this case. Gladding gives a similar explanation, without mentioning the more complete investigations of his predecessors, which would have saved him the trouble of working out the matter for himself. I had already long ago dealt with that difficulty by proposing, in 1889, that method which was afterwards embodied in the "Alkali-Makers' Handbook," viz., precipitating the iron by ammonia, washing the ferric hydroxide, and precipitating the sulphate in the filtrate by barium chloride. Gladding asserts, however, that "the most careful washing failed to wash out all the sulphur from the ferric hydroxide," and he therefore proposes to wash the hydroxide as well as possible and to dissolve it afterwards in diluted hydrochloric acid, thereupon treating that solution with barium chloride; evidently with the tacit assumption that the small quantity of sulphide present in that solution is accurately enough estimated as barium sulphate, in spite of the large quantity of iron present; but that assumption is far from self-evident, nor does it actually represent the truth, as we shall see.

It is quite evident that Gladding, although he knows and quotes the "Alkali-Makers' Handbook," and although he entirely adopts the prescription given there (p. 93) for the *precipitation* of the ferric hydroxide, which deviates not unessentially from those previously given by Fresenius and others, has not completely followed the instructions for the *washing* of the precipitate given immediately after in the following words:—"Filter hot, and wash on the filter with hot water, avoiding channels in the mass, but

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* Read at the Boston Meeting, December 28, 1894.—*Journal of the American Chemical Society*, xvii., No. 3.

so that the whole precipitate is thoroughly *churned up* with the water each time." Many hundreds of pyrites tests made in my own and other laboratories have proved that by following the above instructions the washing of the ferric hydroxide is accomplished in from half an hour to an hour, that the number of washings need not exceed five, and the bulk of the liquid, apart from the original filtrate, need not exceed 100 to 150 c.c., and *that no trace of sulphur is left in the ferric hydroxide*, as evidenced by drying the precipitate, fluxing it with pure soda, dissolving it in water, and testing the solution for sulphate. It is true that the students in my laboratory have sometimes failed to get out all the sulphur, but in *every* case through having washed in the usual way, instead of that described above; and the same men have succeeded in *every* case, after their attention had been drawn to this point.

There is another difference between Gladding's and my own manner of proceeding. I prescribe heating the solution of the sulphate to the boiling-point, as well as that of the barium chloride, adding the latter to the former all at once, allowing to stand for half an hour only, and then at once filtering and washing while the liquid is quite hot. I had convinced myself that under these circumstances the precipitate filters most easily, and no barium sulphate whatever subsequently separates from the filtrate. Gladding, however, not merely adheres to the old and useless prescription of letting the liquid stand over night after the precipitation, but he adds to this a novel and most tedious way of effecting the precipitation, viz., adding 50 c.c. of barium chloride solution quite slowly, one drop per minute. This will take about an hour, instead of a few seconds, as in my method.

I considered it my duty to find out whether the method recommended by Gladding is better than mine, or inferior to it, or equivalent with it; and in the last case, which of the two is easier and quicker to execute. For this purpose a sample of Spanish pyrites was selected which was triturated as usual, and mixed in the most careful manner. The tests were made by one of my demonstrators, H. von Keler, under my constant personal supervision. First of all the sample was tested exactly according to the method laid down in the "Handbook," with the following results:— 50·17; 50·42; 50·20; 50·23; 50·19; average, 50·24 per cent. The insoluble amounted to 1·42 per cent; the moisture to 0·47 per cent. I abstain from reducing the percentages to the dry state, as being unnecessary in this case.

As the next step, a number of samples were decomposed by Gladding's mixture of bromine solution and nitric acid. We found his prescription in this item to be perfectly correct; it is not feasible to hasten the process (which is much lengthier than that used by myself), for instance, by filling the water-bath from the first with hot water. Any attempt to do such a thing ends in an over-violent reaction, and a loss by spurting and separation of free sulphur. We tested, of course, our bromine and potassium bromide, and found them quite free from sulphuric acid.

Three of the samples thus decomposed, according to Gladding, were precipitated exactly according to his method (one hour's precipitation, twelve hours' settling); another three samples according to mine (precipitating all at once and filtering after half an hour). The results were:—

Gladding's Method.	Lunge's Method.
50·24	50·24
50·24	50·22
50·30	50·28
50·26	50·25

We see that both methods of precipitation give identical results, and these also entirely agree with the tests made from the first according to the "Handbook" method, viz., 50·24. The conclusions to be drawn therefrom are:—1. Since both methods of precipitation yield the same result, my expeditious method of precipitation and filtration, which, inclusive of washing, takes about an hour, is preferable to Gladding's method, requiring about twelve hours. 2. Since Gladding's bromine method for decomposing pyrites yields results identical with that prescribed by myself, there is no reason for abandoning the latter and adopting a more tedious method, unnecessarily employing such a disagreeable reagent as bromine.

I understand from a private communication of Mr. Gladding's that he attributes the greatest value to his manner of precipitating the barium sulphate, and that in his opinion by operating in my way barium chloride is always carried down with the sulphate, making the results too high by 0·20 to 0·40 per cent. It would have been most remarkable if that point had been overlooked in the many thousands of tests made according to my methods by perhaps a hundred different chemists; but in order not to incur any reproach, I had this point put to another searching investigation. Mr. W. Jackson made five most careful tests of another sample of pyrites, decomposing and otherwise treating them absolutely in the same way, but making the precipitation in two cases by Gladding's and in three cases by my method. The results were:—

Lunge's Method.	Gladding's Method.
50·59 per cent.	50·60 per cent.
50·63 ,,	50·66 ,,
50·56 ,,	—
Average, 50·59 ,,	Average, 50·63 ,,

This affords another thorough refutation of Gladding's assertion.

In all analyses made up to this point the ferric hydroxide had been precipitated and washed five times exactly in the way described by me; in every case it had been afterwards tested by fluxing with soda, but no trace of sulphur had ever been found. This furnished an additional (although unnecessary) proof that Gladding's assertion in that respect is equally unfounded, and that the treatment described by him (dissolving the ferric hydroxide in hydrochloric acid and precipitating by barium chloride) is quite useless when observing the precautions in washing pointed out by me. Still I thought it advisable to find out how Gladding's process would work in cases where, by some mistake, a little sulphur had been left in the hydroxide, and I grant that in important cases the latter ought to be tested in some way or another for any sulphur left behind. I further grant at once that in this case Gladding's method, as described, is more expeditious than mine: drying the ferric hydroxide, detaching it from the paper, mixing it with pure sodium carbonate, fluxing it in a platinum crucible (in such manner that no sulphur from the gas can get into the mass, *e g.*, in a hole made in asbestos cardboard), dissolving in water, and precipitating the sulphur by barium chloride. It is hardly necessary to say that I did not choose this plan without first considering the very simple method described by Mr. Gladding; but I rejected it, since Fresenius had proved that barium sulphate is very distinctly soluble in an acid solution of ferric chloride. But as Gladding now asserts that the direct solution of the ferric hydroxide in hydrochloric acid yields accurate results, it became incumbent upon me to examine this statement.

Eight samples of our pyrites were decomposed, and the ferric hydroxide was precipitated under absolutely equal conditions of dilution, temperature, and quantities of reagents. The washing was purposely not continued as far as it ought to have been; and as some previous experiments had shown that no uniform degree of exhaustion can be attained by incomplete washing, we estimated in all cases the *total* sulphur, separating, of course, that which was found in the filtrate and that which was left with the ferric hydroxide. Four of the eight samples were treated by Gladding's prescription, and four by my own system. The results were:—

Lunge (fluxing with sodium carbonate).			Gladding (dissolving in hydrochloric acid).		
Filtrate.	Precipitate.	Total.	Filtrate.	Precipitate.	Total.
49·64	0·60	50·24	48·98	1·03	50·01
49·36	1·01	50·37	48·84	1·39	50·23
49·07	1·21	50·28	49·02	1·07	50·19
49·25	1·04	50·29	49·30	0·73	50·03
Average	..	50·29	Average	..	50·09

This proves that Gladding's method does not, in this particular, give accurate, but *low* results (by 0·20 per cent); with less complete washing the discrepancy would evidently have been even greater. The total sulphur found by my process, on the other hand, agrees quite satisfactorily with the correct analyses quoted before.

The final conclusion of this investigation must be:—That in most points Gladding's method is correct, but in *not a single case* more so than my method; his modifications cannot be approved, as they greatly lengthen the time required for the analysis, without any corresponding advantage whatever. In one point which forms the principal novelty in Gladding's process, he is decidedly *wrong*. It is not true that it is unavoidable to leave any sulphur in the ferric hydroxide; on the contrary, this is very easy to avoid. If it has, after all, happened by incorrect manipulation; Gladding's plan will *not* get out all the sulphur, but my plan (fluxing with soda) must be adopted.

I have shown that there is not a single point recommended by Gladding, in deviation from my method, which is fit for adoption, and I must conscientiously advise my brother chemists to adhere to the method just as I have laid it down in the "Alkali-Makers' Handbook."

In conclusion, I would add that I have also tried the method recommended by F. Johnson (Chem. News, vol. lxx., p. 212), omitting to precipitate the iron, but reducing it by sodium hypophosphite to the state of protochloride. Even when working precisely as described by the author, the results were so widely off the truth, that I can make nothing whatever of this plan.

ON THE CORROSION OF ALUMINIUM.

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

In order to ascertain the effects of the weather upon ordinary sheet aluminium, two shallow dishes were made of 1/25 inch gauge metal, of the best commercial quality, and exposed on the roof of the laboratory from Nov. 23rd, 1893, to Dec. 7th, 1894, or fifty-four weeks.

The metal was made into basins so as to catch rainwater, and to give the salts, &c., which it might have in solution, an opportunity to act upon the metal.

The metal very soon lost its brilliancy, and became somewhat rough and speckled with grey spots mixed with larger light grey patches; it also became rough to the feel, the grey parts could be seen to distinctly project above the surface, and under the microscope they presented a blistered appearance. This incrustation is held tenaciously, and does not wash off, neither is it removed on rubbing with a cloth.

The raised parts are probably due to the formation of a hydrated oxide, but I am leaving the determination of the composition of this until I have a larger quantity at my disposal.

Contrary to my expectations, the cups had not lost weight, but had even increased. One, weighing 13·91 grms, had increased by 0·104 grm.; and the other, weighing 13·865 grms., increased by 0·080 grm. After boiling in water for some hours, and rubbing, the first still showed an increase of 0·077 grm., and the second of 0·055 grm.

To ascertain the effects of common salt, a plate of the same metal, 3×4 inches, and weighing 19·829 grms., was repeatedly dipped in a solution of sodium chloride and allowed to dry for three months; this lost 0·019 grm., and, after washing and rubbing dry, 0·059 grm.

One reason for making these experiments is, that Mr. H. C. Russell, C.M.G., F.R.S., the Government Astronomer, some years ago tried aluminium cups for a rain-gauge, but found that they were so quickly corroded through that he had to relinquish the use of the metal (if they had been gilt they might, however, have answered well enough); then, too, it is a very common thing to see aluminium recommended for certain architectural work, on account of its lightness and its assumed permanent lustre; this assumption being due to the statements, repeated from book to book, that aluminium is unaltered by exposure to the air, to the action of water, hydrogen sulphide, and only slightly by dilute acids (even in such works as "Aluminium," by Joseph W. Richards, M A.; London, 1890).

The absolutely pure metal may be permanent in the air, but the best aluminium ordinarily obtainable is in that respect very little, if at all, superior to zinc.

The commercial metal, as we have seen, does not retain its lustre, but very rapidly acquires the appearance of old zinc.

Recently it has been found, also, that aluminium is acted upon by sea-water; it is therefore not so perfect a material for torpedo and other boats as was previously thought.

Hence the prevalent idea that aluminium is a metal resembling gold or silver in the property of not oxidising must be relinquished.

NOTICES OF BOOKS.

City and Guilds of London Institute for the Advancement of Technical Education. Head Office: Gresham College, Basinghall Street. Report on the Central Technical College, Exhibition Road, S.W. Session 1893—1894.

We have to notice with satisfaction the recent change of name of this establishment. Instead of "Central Institution" it is now called more intelligibly the "Central Technical College." A decrease in the number of candidates seeking admission has been observed during the two past years. In 1892 it is remarked the number of candidates for admission was 107; in 1893, 102; and in 1894, only 88. It is pointed out as a consolation that the proportion of the rejected applicants has declined, so that the number actually admitted has not fallen off. We are also reminded that since the College was first opened the facilities for obtaining technical education have been strikingly increased. A further cause, which may or may not be permanent, is the overcrowding of the professions for which a technical training is necessary.

Among the various departments Chemistry, as usual, fares the worst. Of the thirty third-year's students recommended for the diploma of Associate of the Institution, three only had taken Chemistry as their subject.

The difficulty of finding employment for past students is very great, and is, we fear, increasing. "A large proportion of students of the year have only been able to begin their practical career by paying a premium to be received as pupils!" Hence the training received at the College seems to have a minus value in the eyes of employers. This is fearfully disheartening, and goes far to explain the falling off in the number of candidates seeking admission. What is the prospect for youths whose friends are not able to buy them positions in industrial establishments? Perhaps a part of the difficulty springs from the low value which English practical men set upon theoretical knowledge.

A very important feature in this report is that it traces the subsequent career of past students. This is something more worthy to be called "results" than are the lists of pupils advertised by schools as having passed this or that examination. Of these the chemists figure as a small fraction in comparison with the physicists and engineers. If we might suggest, it seems to us that the list of past students might be further improved by the mention of any discoveries or inventions which they have made.

Report on the Result of Investigations on the Micro-Organisms of Sewage. Part I.—Their Relation to those of Sewer Air. Part II.—Observations on the Bacillus of Typhoid Fever and its Relation to Sewage. By J. Parry Laws, F.I.C., and F. W. Andrewes, M.B., M.R.C.P.

These investigations, undertaken by the authority of the London County Council, will prove very valuable contributions to Sanitary Science.

The authors have made a great number of experiments with sewage from the Smithfield outfall from St. Bartholomew's Hospital, from the Fleet sewer, from the Barking outfall, from the Crossness outfall, and from the drain which serves the scarlet or typhoid fever blocks at the Eastern Fever Hospital at Homerton.

The selection of these localities must be pronounced judicious; every care has been taken to obtain fair average specimens of the sewage, and the experiments have been performed *secundum artem.* We may therefore receive the Report with a great degree of confidence.

The conclusions drawn are that sewer air has not the power of taking up micro-organisms from the sewage. The organisms which are most abundant in sewage are precisely those which are absent from sewer air. The authors of course admit that sewage is a common medium for the dissemination of typhoid fever; they consider it possible that polluted soils—*i. e.*, such as have been saturated with sewage—may give up germs to the subsoil air, but the supposition that the air of the sewers plays a part in the conveyance of typhoid fevers seems to them highly unlikely.

A mixture of the four non-pathogenic bacteria did not appear to promote the extinction of *Bacillus typhosus*, but had rather a reverse action. In one flask, which contained the four species *Bacillus fluorescens stercoralis*, *B. fluorescens liquefaciens*, *B. albus putridus*, and *B. cloacæ fluorescens*, some typhoid bacilli were found living even after the lapse of thirty days! This fact certainly does not justify any carelessness in the admission of sewage to drinking waters or articles of food.

We are as yet very far from having eliminated zymotic disease, even from the home-kingdoms.

Researches on the Arseniates, Phosphates, and Modifications of Phosphoric Acid. By Thomas Graham, F.R.S. (1833). Edinburgh: W. F. Clay, Teviot Place. London: Simpkin, Marshall, and Co. (Ltd.) 1895.

This little book forms one of the series of "Alembic Club Reprints," and certainly contains Graham's most important contribution to chemical science. The research here expounded appeared in the *Philosophical Transactions of the Royal Society* for 1833, and certainly, as it is pointed out in the Preface, contained the starting-point of the idea of the Basicity of Acids. It first revealed the mutual relations of the ortho-, pyro-, and metaphosphoric acids, and of their corresponding salts. The author expresses the opinion that there is, indeed, only one phosphoric acid, and that its modifications are due exclusively to the different proportions of water combined with the acid. The recognition of their distinctive characters was very fruitful, and has led the way to important results.

CORRESPONDENCE.

DE BOISBAUDRAN'S SYSTEM.

To the Editor of the Chemical News.

Sir,—From time to time chemists have been edified or tantalised with references to or promises of a "system" which M. Lecoq de Boisbaudran has elaborated, but which seems not yet ripe for publication. May we hope from a paper in the *Comptes Rendus*, which you have reproduced in the last number of the Chemical News, that the distinguished author will at last break silence and give the scientific world an opportunity of judging on the real scope and the capabilities of this long promised system?—I am. &c.,

J. W.S.

"YEAR-BOOK OF PHARMACY."

To the Editor of the Chemical News.

Sir,—In the *Year-Book of Pharmacy*, 1871, p. 628, the Chairman of the Dinner of the Pharmaceutical Conference, in introducing the toast "Success to the British Pharmaceutical Conference," stated "Last year the Conference issued the *Year-Book of Pharmacy*.—(Cheers). The Chemical Society has already copied our example; and those who were present at the inaugural address of Sir William Thomson last night are aware that a similar undertaking is proposed to be carried out by the British Association." Dr. Alexander Wood mentioned this matter too (p. 630).

Although knowing much of the publications of most of the Chemical and allied Societies, I know nothing of either of these works, and should be glad if some correspondent can give me any information respecting them. The reference cannot be to the Journals of the two Societies, for both had been running many years previous to 1870.—I am, &c.,

J. Cuthbert Welch.

The Laboratory, The Brewery,
Reading, March 3, 1895.

BORON CARBON BATTERY.

To the Editor of the Chemical News.

Sir,—Mr. H. N. Warren (Chem. News, lxxi., p. 87) asks me where I "obtained the information from as regards the existence of a platinum element" in his battery, "while at the same time the title of the battery is distinctly stated 'the boron carbon battery.'" I will say, in reply, that my only source of information was his own description in the Chemical News (vol. lxxi., p. 2). The information was not contained in the "title of the battery," and I did not look for it there. It is contained in the following sentence:—"The cells themselves are constructed on the flat system, with sliding carbon plates enclosed in teak-wood boxes, the carbons being chemically prepared by special treatment, whereby gaseous compounds of boron are so decomposed as to allow of the boron becoming absorbed into the pores of the carbon, which are afterwards soaked in solution of oxalate of platinum, and heated to redness in an atmosphere of hydrogen." If Mr. Warren can make carbon elements by this process that do not contain a considerable quantity of platinum he has wrought a greater "revolution" in chemistry than any he has yet pointed out in voltaic electricity.

My former criticism was not intended to disparage Mr. Warren's efforts, as he seems to suppose, but rather as an expression of regret that he did not, in connection with his claims, give some intelligible data from which it would be possible to compare his battery with others, as he does not describe the battery so that others could prepare it and verify the results. The only datum he gives is that the electromotive force is 3 volts. This in itself is nothing remarkable, nor does it signify any revolution in voltaic electricity. He adds the very ambiguous statement, " and giving a constant current from 2 to 2·5 for an almost unlimited duration." The natural inference is that he means 2 to 2·5 ampères. If he means that he obtains a constant current of 2 ampères for more than about 188 hours by the consumption of one pound of zinc, it means perpetual motion. If he means that he obtains 2 ampères for 188 hours or something less by the consumption of one pound of zinc, then he has not accomplished anything revolutionary.

The question of most importance, it seems to me, is not whether this is a " Yankee bull " or an " English calf," but whether Mr. Warren is going to revolutionise voltaic electricity. I invite him again, therefore, if he has anything further to say on the subject, to give at least some definite data showing what his battery will do.—I am, &c.,

C. J. Reed.

441, Chestnut St., Philadelphia.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 8, February 25, 1895.

Ebullioscopic Study of certain Colouring Derivatives of Triphenylmethane.—A. Haller and P. Th. Muller.—The authors refer to the discussion concerning these compounds. Some chemists, such as O. and E. Fischer, Nietzki, Bernthsen, &c., imbued with the very seducing theory of the chromophoric groups introduced by O. Witt, ascribe the function of the colouring basic derivatives of triphenylmethane to the presence of a quinonimide group. Rosenstiehl, on the contrary, ascribes the tinctorial function of these compounds to the para-positions occupied by the groups $Ar_2(R=H,CH_3C_2H_3\ldots)$, to the central methanic carbon ; and second to the union to this same methanic carbon of an element or a group of a function opposite to that of the group introduced into the benzenic nucluei. The only conclusion which the authors have been able to draw is that the hydrochlorates of the tinctorial matters of the amidotriphenylmethane group are not dissociated, whilst the ammonium chlorides and the nitrosodimethylaniline hydrochlorate are so most distinctly.

The Academy proceeded to nominate a foreign associate, *vice* the late Herr Kummer. Herr Weierstrass was elected with a majority of 43 votes, as against Professors Frankland and Huxley, who received each one vote.

E. Carvallo addressed a letter concerning a " sealed paper " concerning the theoretic establishment of the laws of theoretic absorption, and announced the early production of a memoir on the subject.

Dr. L. L. de Koninck addressed to the Academy a reclamation of priority concerning the properties of nickel and cobalt sulphides.

Reduction of the Congelation-point of very Dilute Solutions.—A. Leduc.—This paper does not admit of useful abstraction.

On a Sensitive Pressomètre (!) for Measuring the Pressures of Liquids.— Paul Charpentier. — This memoir requires the accompanying figure.

Measurement of the Intensity of Light by the Chemical Action produced. Experiments with Mixtures of Ferric Choride and Oxalic Acid.—Georges Lemoine.—The decomposition by light of mixtures of oxalic acid and of ferric chloride (*C. R.*, cxii.) may be utilised for measuring the luminous intensity; the greater it is found, the more rapid is the chemical transformation. The author finds that the heat liberated does not in reality disturb the results, and that the decompositions cease immediately on the suspension of the light. The natural light of the sun in summer, passing through a stratum of solution of potassium chromate of 25 m.m. in diameter varied in intensity from 0·001 to 0·007. If passed through blue glass, and through a layer of 25 m.m. of a solution of copper sulphate it was 0·40 to 0·50.

Certain Compounds of Lead Iodide with other Metallic or Organic Iodides.—A. Mosnier.—But few of the compounds formed by lead iodide with the metallic and the organic iodides are hitherto known. The author has obtained a double lead and ammonium iodide, $3PbI_2,4NH_4I,6H_2O$. Lead iodide forms double iodides with the tetramethylammonium, the tetraethylammonium, and phenylammonium iodides. The double sodium iodide obtained by the author has the composition $2NaIPbI_2,4H_2O$, whilst there crystallises out from the mother-liquor another compound, $2NaIPbI_26H_2O$. The double iodides of lead and lithium, and those of lead and the alkaline-earthy metals, and of the magnesium series, have also been obtained and examined.

Some Compounds of the Nitric Oxides with the Iron Chlorides.—V. Thomas.—On passing nitric oxide through a solution of ferric chloride at the ordinary temperature there is obtained a compound, Fe_2Cl_6NO ; if the same experiment is conducted at 60°, there is produced $2Fe_2Cl_6NO$ as a red powder. A compound, $FeCl_2NO+2H_2O$, is obtained in black crystalline needles. Another compound, $FeCl_2NO$, forms small yellow crystals.

Action of Formic Aldehyd upon Hydroxylamine Hydrochlorate and Monomethylamine Hydrochlorate.—A. Brochet and R. Cambier.— This paper does not admit of useful abstraction.

The Active Amylic Ethers.—Ph. A. Guye and L. Chavanne.—The authors arrange their results in four tables.

MISCELLANEOUS.

The John Scott Legacy and Premium.—We learn that Messrs. Cross and Bevan and Clayton Beadle, of London, have been awarded the John Scott Legacy Medal and Premium, by the Franklin Institute, for their " Discovery of a new Plastic Compound of Cellulose."

The Chemical Laboratory of Wiesbaden.—In the Winter Term 1894-95 there were fifty-six students on the books. Of these, thirty-three were from Germany, four from England, four from North America, three from Norway, three from Holland, two from Switzerland, one from Italia, one from Austria, one from Belgium, one from Sweden, one from Denmark, one from Russia, and one from Australia. Besides the Director, Geh. Hofrath Prof. Dr. R. Fresenius, there are engaged, as Teachers in the Establishment, Prof. Dr. H. Fresenius, Prof. Dr. E. Borgmann, Dr. W. Fresenius, Dr. E. Hintz, Dr. med. G. Frank, Dr. W. Leng, and Architect T. Brahm. The next Summer Term begins the 24th of April. During the last term, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory and the Versuchsstation, on behalf of manufacture, trade, mining, agriculture, and hygiene.

Camera Club Photographic Conference, 1895.—The 1895 Conference will be held at the Camera Club, Charing Cross Road, on Tuesday and Wednesday, April 2nd and 3rd, under the Presidency of Captain W. de W. Abney, C.B., R.E., D.C.L., F.R.S., P.R.A.S.

On Tuesday, April 2nd, at 4 p.m., the President will open the Conference at the Club, and Papers will be read from 4 to 6 p.m. At 8 p.m. the Conference will be continued, and Papers will be read from 8 to 10 p.m.

On Wednesday, April 3rd, at 4 p.m., the Conference will be renewed, and Papers will be read from 4 to 6 p.m. At 8 p.m. the Conference will be continued and Papers will be read from 8 to 10 p.m.

On Thursday, April 4th, at 7.30 p.m., the Annual Dinner for Members and Friends will be held.

On Monday, April 8th, a Lantern Slide Exhibition will be given at the Society of Arts (by kind permission of the Council), and for this special tickets will be required.

The Members' Annual Exhibition of Photographs will be commenced at the Club on the first day of the Conference. A complete programme will be issued later and distributed. Visitors are cordially invited to take part in the discussions. Tickets of admission may be obtained through any Member of the Club, or on written application to the Secretary.

Recognition of Arsenic in Textile Goods, &c., in Sweden.—According to the Swedish law (April 10th, 1885) the sale of the following articles is forbidden:—Paper-hangings, curtains, carpets, Venetian blinds, artificial flowers, and other wares printed or painted from water-colours (glue, gum, starch, dextrine, albumen, &c.) with arsenical pigments, if from 200 square centimetres of the object a brown or black-brown arsenical spot can be obtained which is at least partially opaque. The arsenical spot is to be produced by the reduction of arsenic sulphide with potassium cyanide and sodium carbonate, and the reduction tube must have an internal diameter of 1½ to 2 m.m. The same law holds good for tissues, yarns, lamp-screens, sealing-wax, wafers, stearine, or other candles; if in case of tissues and lamp-screens 100 square centimetres, and in case of other articles 21 grms., yield an arsenical mirror. According to the decree, in the report on the percentage of arsenic in the goods the weight or surface of the article used for investigation is to be mentioned, and there must be enclosed along with the arsenical mirror a piece of the tissue examined of at least 500 square centimetres on which all the colours present are represented. The tube enclosing the arsenical mirror must be melted at both ends. Both the specimen of the tissue and the arsenical mirror are to be sealed to the report or to a paper bearing the name of the analyst, and a number which is quoted in the report. The execution of the analysis according to the agreement of the Swedish commercial analysts is to be as follows:—A flask of the capacity of about 300 c.c. is connected with an open receiver by means of a 50 c.c. pipette, bent twice at a right angle, first upwards and then downwards. The receiver contains about 100 c.c., and is half filled with water, into which the point of the pipette dips slightly. The sample is placed in the flask along with 2 grms. non-arseniferous ferrous sulphate, and covered with 50 to 80 c.c. of concentrated hydrochloric acid free from arsenic, of sp. gr. 1·18 to 1·19. In case of bronze colours or other metallic articles there are added from 2 to 3 grms. of ferric chloride free from arsenic. The flask is heated and the hydrochloric acid is kept in ebullition as long as the pipette can be grasped with the hands. The distillate obtained is mixed with 50 c.c. of saturated sulphuretted hydrogen water, and diluted with 50 c.c. of water, and hydrogen sulphide is introduced. The arsenic sulphide deposited is allowed to stand for twelve hours, filtered through a small filter, washed until free from an acid reaction, and then dissolved in 5 c.c. of dilute ammonia (1 vol. ammonia of sp. gr. 0·96 and 1 vol. of water). The solution after the addition of 0·02 grm. sodium carbonate is evaporated to dryness on a watch-glass, the residue ground up with 0·3 grm. of a mixture of dry sodium carbonate and potassium cyanide, and reduced in a non-arsenical bulb tube in a current of carbonic acid. The bulb tube is so constructed that the narrow part in which the arsenical mirror is to be deposited joins close to the bulb of 2 centimetres in diameter.—*Zeitschrift fur Analyt. Chemie*, 1895, p. 88., and *Kemiska Notiser*.

MEETINGS FOR THE WEEK.

Monday, 18th.—Society of Arts, 4. (Cantor Lectures). "Commercial Fibres," by Dr. D. Morris.

Tuesday, 19th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 8. "Practical Carpet Designing," by Alexander Millar.

Wednesday, 20th.—Society of Arts, 8. "The Progress of the Abattoir System in England," by H. F. Lester.
— Geological, 8.
— Meteorological, 8.
— Microscopical, 8.

Thursday, 21st.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Three Periods of 17th Century History—III. The Restoration," by Samuel Rawson Gardiner, M.A.
— Chemical, 8. "Studies in Isomeric Change—III. The Ethylbenzenesulphonic Acids," by Dr. G. T. Moody. "Some Oxypyridine Derivatives," by Miss Sedgwick and Dr. Collie. "Colouring Principle of *Toddalia aculeata* and *Evodia meliæfolia*," by A. G. Perkin and J. J. Hummel.

Friday, 22nd.—Royal Institution, 9. "Emily Brontë," by Sir Wemyss Reid, LL.D.
— Physical, 5. (At the Royal College of Science, South Kensington). "Objective Reality of Combination Tones," by Prof. A. W. Rücker, F.R.S., and Mr. Edser. "Some Acoustical Experiments," by Dr. C. V. Burton. "Use of an Iodine Voltameter," by Mr. Herroun.

Saturday, 23rd.—Royal Institution, 3. "Waves and Vibrations," by Lord Rayleigh, F.R.S.

A GUIDE TO STEREOCHEMISTRY, with an INDEX TO THE LITERATURE. By Arnold Eiloart, Ph.D., B.Sc. (Lond.). Illustrated with Fifty Woodcuts and Five Plates. 8vo. 4s. post free. [1893.

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Although no new branch of chemistry is found more interesting by chemists and students than that which treats of the arrangement of atoms in space, so that lectures on the subject are everywhere welcome, yet it has been difficult to give guidance and permanence to this interest for want of a suitable text-book. It seemed desirable, in attempting to supply such a book, to make it as compact as possible without stripping the subject of the charm so natural to it. In this Guide, therefore, established facts have been promptly accepted as such. More than the usual proportion of space is occupied by the later and more daring developments of stereochemistry; the theories concerning the space relations of nitrogen are a case in point. At the same time especial care has been taken to notice the criticisms of those hostile to such innovations.

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LECTURES.

Experimental Chemistry (Inorganic)	Prof. H. FRESENIUS, Ph.D.
Experimental Physics .. .. Stöchiometry	W. FRESENIUS, Ph.D.
Organic Chemistry..	E. HINTZ, Ph.D.
Chemical Technology	Prof. E. BORGMANN, Ph.D.
Microscopy, with exercises in Microscopic work	W. LENZ, Ph.D.
Chemistry and Analysis of Foods ..	Prof. H. FRESENIUS, Ph.D. Prof. E. BORGMANN, Ph.D. W. FRESENIUS, Ph.D., and E. HINTZ, Ph.D.
Hygiene .. .. Practical exercises in Bacteriology..	Dr. med. G. FRANK.
Technical Drawing, with exercises ..	J. BRAHM.

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. Kreidel's Verlag, at Wiesbaden, or to the undersigned.

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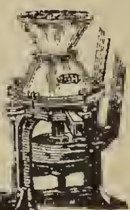

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THE CHEMICAL NEWS.

Vol. LXXI., No. 1843.

ARGON.

At the meeting of the French Académie des Sciences on Monday, March 11th, M. Berthelot announced that, having received from Dr. Ramsay a small specimsn of the new gas, he had submitted it to several experiments, and had found that it could enter into combination with certain organic compounds, especially with the vapour of benzene, under the influence of the silent electric discharge. He promised to publish next week the details of this experiment.

LIQUEFACTION OF HYDROGEN.

We learn that Professor Olszewski has liquefied hydrogen. Its critical point, measured with a platinum resistance thermometer, is $-233°$ C., and its boiling-point at atmospheric pressure is $-243.°$

THE EXISTENCE OF AN ELEMENT WITHOUT VALENCY OF THE ATOMIC WEIGHT OF "ARGON" ANTICIPATED BEFORE THE DISCOVERY OF "ARGON" BY LORD RAYLEIGH AND PROF. RAMSAY.

By Lieut.-Col. SEDGWICK, late R.E.

The conclusion that inactive elements exist, or once existed, follows necessarily from the train of reasoning adopted by me in my book "Force as an Entity," published in 1890.

But before showing that my book contains a recorded anticipation of the existence of an element without valency of the atomic weight of "Argon," or rather of atoms of that kind, for the term Element seems to suggest the idea of something capable of combining, and I did not use it, I wish to make a few remarks in regard to the realistic view of Matter and Force, which enabled the existence of "Argon" to be thus, as it were, predicted.

The atoms are, of course, Newton's "solid massy hard impenetrable movable particles" of certain "sizes and figures," "so very hard as never to wear or break in pieces." And lines of force are viewed as Clerk-Maxwell viewed them in his paper "On Faraday's Lines of Force," though I was not aware that he had viewed them in that particular way when I wrote my book.

In that paper Clerk-Maxwell treats lines of force "not as mere lines, but as fine tubes of variable section carrying an incompressible fluid," and obtains supplies of the fluid by "sources where the fluid is created, and sinks where it is annihilated," and then gives mathematical investigations of some of the simplest problems in electricity and magnetism.

But in his paper "On Physical Lines of Force" he tells us that the conception he made use of was that of "currents in a fluid."

Now the view that lines of force are currents in an incompressible fluid is precisely the view taken in my book; but I have extended the fluid analogy so as to utilise the other fluid forms, namely, the pool, the film, and the wave.

By bringing matter in the form of atoms into the field to supply an "allurement" to which the fluid, with an overpowering tendency to attach itself to matter, will yield, so far as to overflow from its pools in fine streams upon atoms of matter, I am able to use pools as natural substitutes, both for the "sources" capable of creating the fluid from nothing, and for the "sinks" capable of annihilating it, with which Clerk-Maxwell worked and made his views unreal; and then I am able to proceed, for the fluid not only supplies by its currents a means of transporting atoms and bringing them together, but it also supplies by its films a binding material to bind atoms together in molecules, and molecules in masses, as shown by the binding power of a film of water between two clean sheets of glass and of water of crystallisation in a crystal.

If, then, we can get a form for the atom which will limit and define, in accordance with its valency, the ways in which other atoms can be bound on to it by films of the fluid, we shall plainly arrive at a natural and real explanation of chemical combination and valency.

Now, our ordinary every-day experience of the steadiness of things resting on flat surfaces, and of the unsteadiness of things resting on rounded surfaces, tells us that the form we are in search of is supplied by a sphere with flat places on its surface.

For we know that two bodies which are perfectly spherical in form cannot be united by a film, but will roll upon each other. If, however, the spheres have, both of them, large flat places on their surfaces, then they can be firmly united by a film by bringing their flat places together. And if one of the spheres has two such flat places on its surface, then two other spheres with flat places—and not more than two—can be united to it; or if it has three such flat places, then three other spheres with flat places—and not more than three—can be united to it; and so on.

By making the number of flat places correspond with valency, we get in the sphere with flat places on its surface an exact form for the valent atom. We also get, as a necessary consequence, a form for the non-valent atom, namely, that of a perfect sphere; and thus non-valent elements come in naturally and necessarily with this explanation.

But these are the precise views in regard to Force and Matter which are developed in "Force as an Entity." Chapter III. in that book deals with the form of the atom under the conception that the form of the valent atom is that of a chipped sphere with flat places on its surface corresponding in number to the valency of the atom, so that the monovalent atom has the form of a sphere with one flat place; a divalent that of a sphere with two flat places; a trivalent that of a sphere with three flat places; and a tetravalent that of a sphere with four flat places; and also that atoms in the form of perfect spheres can have no valency.

In that chapter it is shown in effect that the atomic weights of the whole of the metalloid elements afford most remarkable confirmation of the correctness of this view in respect of their hydrogen valency, since they run in series each of which contains a monovalent, a divalent, a trivalent, and a tetravalent member. And, moreover, these series are such that the atomic weights of all the members of a series can be obtained from the atomic weight of a single non-valent element, by cutting off from the atomic weight of the non-valent one portion weighing 2 to obtain the atomic weight of the monovalent, two portions weighing each 2 to obtain that of the divalent, three to obtain that of the trivalent, and four to obtain that of the tetravalent.

This is shown most remarkably by the first of these series, which runs thus:—

$$\mathrm{Fl}^{\mathrm{I.}},\ 19;\ \mathrm{O}^{\mathrm{II.}},\ 16;\ \mathrm{N}^{\mathrm{III.}},\ 14;\ \mathrm{C}^{\mathrm{IV.}},\ 12,$$

and is such that the atomic weights of all the members can be obtained in the way explained from a non-valent of atomic weight 20, as shown at pp. 60 and 61, of "Force as an Entity."

Thus $20-2\times1=18$ gives the atomic weight of the monovalent fluorine.
$20-2\times2=16$ that of the divalent oxygen.
$20-2\times3=14$ that of the trivalent nitrogen.
$20-2\times4=12$ that of the tetravalent carbon.

Now the atomic weights of all the members of this series plainly accord almost exactly with the view that they have atoms in the form of chipped spheres with one flat place in the case of the monovalent fluorine, two in that of the divalent oxygen, three in that of the trivalent nitrogen, and four in that of the tetravalent carbon, and that all are derived from a non-valent element with perfectly spherical atoms weighing each 20 by a process of chipping in which a portion weighing 2 is detached in making each flat place. For the monovalent fluorine atoms with one flat place ought in that case to weigh 18, the divalent oxygen atoms with two flat places 16, the trivalent nitrogen atoms 14, and the tetravalent carbon atoms 12; and these are their actual weights, in round numbers, with the exception only of the fluorine atom, the weight of which is 19 instead of 18.

In showing thus the correctness of our conclusions in regard to the form of the atom, we incidentally arrive at a determination of the atomic weight of one of the elements without valency, namely, of one of atomic weight 20, with atoms in the form of perfect spheres, with which we have all along been working, in the way shown at p. 61 of "Force as an Entity."

The three other metalloid series all point in the same direction, though not quite so satisfactorily as the first, and from them we can arrive in the same way at determinations of the atomic weights of three more elements without valency, and obtain the following values, viz., 37, 82, and 129.

This, too, is done in the Ideal and Real Tables and context at pp. 64 and 65 of "Force as an Entity," but the values obtained are not 37, 82, and 129, but 40, 80, and 120, in recognition of the closeness with which three, namely, 20, 37, and 82, out of the four values obtained in this way approximate to multiples of 20.

In this way, then, the existence of an element of atomic weight 40 having atoms in the form of perfect spheres, which are stated at the top of p. 66 to be "unaffected either by chemical affinity or cohesion," was determined from the series—

$$\mathrm{Cl^{I}},\ 35\cdot5;\ \mathrm{S^{II}},\ 32;\ \mathrm{P^{III}},\ 31;\ \mathrm{Si^{IV}},\ 28,$$

in connection with the other metalloid series, and the element tabulated in the Ideal Table at p. 64.

And thus an inactive element is tabulated, which agrees exactly with "argon," taking the atomic weight of argon in round numbers as 40.

It will be seen that though the determination of the atomic weight of this element without valency, which agrees exactly with argon, is only given incidentally, yet that the whole argument in connection with which it is given hangs upon the existence of elements without valency with atoms in the form of perfect spheres, and postulates the existence of such elements, though not necessarily in the present, because they may all have been converted by chipping into valent elements. Other considerations, however, come in to show the probability of the existence of such elements in the present day.

For we require in order to fill interstellar space a medium which, while transmitting gravitation, will offer little resistance to the motions of the heavenly bodies traversing it. And such a medium is supplied by elements without valency with the fluid with which we have been working, since, being unaffected by cohesion or chemical affinity, they will offer little resistance to the motions of the heavenly bodies while transmitting gravitation freely.

There was therefore not only a need for elements without valency in the past, but there is also a need for them in the present.

Accordingly the possibility that elements without valency, or rather the atoms of such elements, are in actual existence at the present day, and moreover that their atoms "are thickly distributed throughout space in the intervals between the heavenly bodies large and small," is pointed out at pp. 68 and 69 of "Force as an Entity."

"Force as an Entity" represents, however, only a preliminary statement of my conclusions, and at the same time a hurried statement because the inquiry was cut short by the expiration of the furlough which enabled it to be undertaken. It is therefore incomplete, and in many ways unsatisfactory.

I have since continued the investigation whenever time was available, and have obtained further results tending to improve and strengthen the case in every way.

I am now able to show in the same way that while the form of the metalloid atom is that of a sphere with flat places formed by cutting down the surface and thus reducing its weight, that of the metal atom is, on the other hand, a sphere with flat places formed by building up the surface, and thus making elevated flat places or flat-topped excrescences upon it, and adding to its weight.

Accordingly we have metal series showing gain in valency, attended with *gain* in atomic weight, corresponding exactly to the metalloid series, which show, as we have seen above, gain in valency, attended with *loss* in atomic weight.

Moreover we have both kinds of these series derived from the same element without valency in four cases, so that the metal series point just as strongly as the metalloid series to the existence of four elements without valency of atomic weights 20, 37, 82, and 130, in addition at least to four others of atomic weights 5, 62, 105, and 201 respectively.

These results were embodied by me in a paper which was sent to the Royal Society in November, 1892, and in another direction in the following December, and may perhaps be recollected by someone.

I am now able also to get over the difficulty arising from the marked difference between hydrogen and chlorine valency shown by some of the metalloid elements by pointing out that with large chlorine atoms abnormal valency may be expected to occur from molecules being caught and held without being regularly seated on flat places, and that the validity of this explanation is shown by the recognised fact that chlorine valency differs from hydrogen valency usually by molecules and not by simple atoms.

I have embodied these and other results of further investigation in another book which I had actually sent round to several publishing firms for consideration before the news of the discovery of argon reached me and rendered revision necessary.

3, Alexandra Road, Epsom,
March 15, 1895.

ABBREVIATED NAMES FOR CERTAIN CRYSTAL FORMS.*

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

When the names of crystals have to be used constantly, as in lecturing upon or speaking about crystals and minerals, the waste of time involved by the present sesquipedalian names is a very serious matter, and it appears to me that it is desirable to shorten them somewhat. I therefore venture to propose the following curtailed names for certain crystals to be used ordinarily, although not always, in place of the descriptive terms now in use. It is not expected that these "short titles" will supersede

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* Read before the Aust. Assoc. for the Advancement of Science, Brisbane, January, 1895.

the older descriptive terms, but for conversational purposes they may prove useful.

The third column shows the number of letters saved in each case.

In every instance sufficient of the roots of the full name have been retained to indicate the source and meaning of the proposed abbreviated terms.

Abbreviated Names for Crystals.

Name.	Abbreviated name.	Saving of letters.
Octahedron	Octron	4
Hexahedron	Hexron	4
Rhombic dodecahedron	Rho-dodecron	8
Triakis octahedron	Tri-octron	8
Icositetrahedron	Icotetron or Icositetron	7 or 5
Tetrakishexahedron	Tetrahexron	7
Hexakisoctahedron	Hexoctron	8
Tetrahedron	Tetron	7
Trigonal-dodecahedron	Tri-dodecron	9
Deltoid-dodecahedron	Del-dodecron	8
Hexakistetrahedron	Hexatetron	8
Pentagonal-dodecahedron	Pentron or Pentadodecron	15 or 9
Trapezohedron	Trapezron	4
Tetragonal Pyramid	Tetramid	9
Ditetragonal Pyramid	Ditetramid	10
Tetragonal Prism	Tetrism	8
Ditetragonal Prism	Ditetrism	8
Sphenoid	Sphenoid	0
Scalenohedron	Scalenron	4
Hexagonal Pyramid	Hexamid	9
Dihexagonal Pyramid	Dihexamid	9
Hexagonal Prism	Hexism	8
Dihexagonal Prism	Dihexism	8
Rhombohedron	Rhomdron	4
	Total ..	174 or 166

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending February 28th, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 10th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 58 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, as far as possible, from Feb. 1st to Feb. 28th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 58 samples examined one was recorded as "slightly turbid" and four as "clear but dull," the remainder were clear, bright, and well-filtered.

The unprecedented frost which visited the Thames valley during the month of February has prevented many samples being drawn for analysis, and it is difficult to make any fair comparison between the chemical composition of the waters during last month and the corresponding month last year, or with the months of December and January just preceding. It will therefore be sufficient to say that in every respect the freedom from pollution is of a very high character, the organic carbon and the brown constituent of the colour having diminished to about one-half the usual figures.

Bacteriological observations have been carried on during the whole of the month. Performing the operations in exactly the same manner as we have been accustomed to do them from the commencement, so as to admit of the results from month to month being strictly comparable among themselves, and keeping the culture plates incubating for 48 hours, the waters from the general wells have an average of 44 bacteria per cubic centimetre, that from the river at Hampton Court before filtration containing 7334.

Many localities in the South-east and East districts of London having had their service pipes frozen, the water from Aldgate pump was largely resorted to for domestic purposes. This has been for many years supplied from the New River Company, and it may interest consumers to know that analysis shows that the pump water is very pure, and is identical in composition with New River water from other localities. It was found to contain 133 microbes per cubic centimetre.

February has been a remarkably dry month. The rainfall (including snow) has only amounted to 0·21 inch, whereas the mean for the last twenty-five years for this month is 1·92, showing the large deficiency of 1·80 inch.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

SYNTHETIC EXPERIMENTS IN THE PYRAZOL SERIES.*

Part I.

By R. von ROTHENBURG.

L. Knorr, in a long series of brilliant experimental researches, has studied the oxygenated derivatives of pyrazol, as also those derived from phenylhydrazin, the pyrazolones, and pyrazolidones. In a series of short treatises in the Berlin *Berichte* I have given communications on the preparation of pyrazolon and its simplest derivatives, which I now give more fully in connection.

1. Pyrazolon is formed on the distillation of the calcium salt of (3)-carbon acid by oxidation of pyrazolidon, by means of the hydrazin hydrate from propiolic acid or its esters, from cumalic acid and β-aldoximacetic acid or their esters.

Pyrazolon forms a readily mobile liquid, turning yellow on exposure to light, and of very intense characteristic odour. It does not solidify in a freezing mixture, and boils at a pressure of 759 m.m. at 156—157°. It is very unstable in contact with concentrated hydrochloric acid, being completely decomposed at 100° into humoid substances, no hydrazin being split off. The ordinary organic solvents take it up very readily; even water dissolves it in appreciable quantity. Its specific gravity is 0·9137 at 16·5°. Its composition is $C_3H_4N_2O$. It dissolves in acids and alkalis, and forms salts with them. In the latter, pyrazolon passes doubtless into the form of an oxypyrazol.

The pyrazolon silver salt is precipitated from an ammo-

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* From the *Journal Praktische Chemie*.

niacal solution of pyrazolon as a white curdy precipitate, little sensitive to light, $C_3H_4N_2O,C_3H_3AgN_2O$. Other metallic salts precipitate the solution of pyrazolon, calcium, and barium chlorides white, copper sulphate a yellowish green, nickel sulphate an apple-green, and cobalt salts a peach-blossom. Platinum chloride throws down a very unstable yellow double salt.

(4)-Benzalpyrazolon is formed on boiling together equivalent quantities of pyrazolon and benzaldehyd. Its physical properties are very unpleasant. The semi-solid mass has a purple-red colour.

(4)-Isonitrosopyrazolon is obtained on passing nitrous acid (avoiding any excess) into a dilute alcoholic solution of pyrazolon. It and its following compounds have very intense colouration, especially if subsequently shaken out with ether, which shows a pure yellow or blood-red colour, and permits of (like the reaction with ferric chloride) the recognition of the smallest traces of pyrazolon in large volumes of liquid.

The nitroso-substance is strongly acid, and is easily or freely soluble in the ordinary solvents.

The pyrazolon-(4)-isonitro-silver salt is precipitated from the bluish red ammoniacal solution of isonitropyrazolon by silver nitrate (accurately neutralised) as a reddish yellow granular powder. It detonates if suddenly heated.

(4)-*p*-azotoluolpyrazolon is formed if a dilute solution of the para-diazotoluol salt is allowed to run into a feebly alkaline solution of pyrazolon, stirring well.

The new derivative crystallises from alcohol in small, splendid iridescent, purple-red leaflets, fusible at 219°. It is suitable for an approximate determination of pyrazolon in an aqueous solution. On reduction it behaves like a true azo-compound. Its composition is $C_{10}H_{10}N_4O$.

The (4)-azobenzenepyrazolon was obtained in an analogous manner as a well-crystallised substance, fusible at 185°.

Pyrazolon-(3)-carbon acid is formed on the saponification of its esters. The ethyl-ester is boiled for some time with concentrated hydrochloric acid until completely dissolved, the excess of acid is expelled by repeated evaporation with alcohol, and the substance is re-crystallised from dilute spirit. Its composition is $C_4H_4N_2O_3$. It forms two series of salts: neutral, in which only the carboxyl-group has a halogenous action, and basic, which have a (5)-oxypyrazol constitution.

The author describes the neutral, sodium, ammonium, and copper salts, and the basic pyrazolon-(3)-carbon, calcium, and silver salts, the latter of which has the composition $C_3H_2N_2OAg{\cdot}COOAg$.

(4)-Benzalpyrazolon-(3)-carbon acid is formed by heating the carbon acid for some hours with the calculated quantity of benzaldehyd to 120—130° in an oil-bath. It is sparingly soluble in ordinary solvents, but readily with a yellow colour in ammonia and alkalis. It separates from alcohol as a granular powder, fusible at 243°. Its composition is $C_{11}N_8N_3O_3$.

(4)-Isonitrosopyrazolon-(3)-carbon acid is best obtained by passing gaseous nitrous acid into the carbon acid washed up with alcohol, in which it dissolves with a deep red colour. The strongly acid nitroso-compound dissolves with a red colour in glacial acetic acid and caustic alkalis, but from ammonia with a violet colour. It crystallises from alcohol in golden yellow leaflets, which decompose at 215—219°. Its composition is $C_4H_3N_3O_4$.

The silver salt of the above acid,—

$$C_3H_2N_2ONOAgCOOAg,$$

is obtained by cautiously precipitating with a solution of silver nitrate the ammoniacal solution of the nitroso-compound previously mixed with solution of silver nitrate. It is an orange-red granular precipitate, which detonates slightly if heated.

Azobenzenepyrazolon-(3)-carbon acid, $C_{10}H_8N_4O_3$, is formed by running the calculated quantity of a diazobenzene salt into the alkaline solution of the carbon acid, refrigerating and stirring well. The colouring matter is very sparingly soluble, strongly acid, and forms a fiery-red granular powder, fusible above 250° with decomposition.

(To be continued).

THE CHEMOMETER.*

By W. OSTWALD.

If we bear in mind the general property belonging to every kind of energy, *i. e.*, that there is a certain magnitude (I call it, with Helm, intensity) the equality or inequality of which determines whether the energy in question is in equilibrium or not, we are led to a remarkable result as regards chemical energy. We must expect that, as there exist measuring-instruments for such magnitudes of intensity as temperature, pressure, and electric potential, which allow us to read off directly or indirectly the numerical value of these magnitudes, so there must be producible such a measuring-instrument for the intensity of chemical energy. Just as the thermometer enables us to determine directly for heat, the manometer for volume-energy, or the electrometer for electric energy, whether two regions on their immediate contact will be in thermic, mechanical, or electrical equilibrium, or not, there must be a "chemometer," by the application of which to two substances or complexes of matter we should ascertain whether chemical equilibrium exists between them or if a reaction would ensue when they are brought in contact.

In order to reply to the question whether such a chemometer exists or can exist, we must first consider the nature of chemical energy somewhat more thoroughly. But I may already remark that there is certainly hitherto no universal chemometer; but for a large class of chemical processes, including the most important, there is such a measuring-instrument which allows us to decide whether, and in what direction, a chemical action will ensue between two given substances.

Of course I am prepared to be told, on behalf of "pure chemistry," that we need nothing of the kind; we have simply to try. I must admit that I have as yet no conception of the possible practical application of the chemometer.

We have, in the first place, to take up the questions, What is chemical energy? and what are its factors?

The quantities of energy which are evolved or taken up in chemical phenomena, *i. e.*, in the transformation of given substances into others with different properties. It is presupposed that the energies do not change, or that such changes, if they occur, are taken into account.

We see, from this definition, that we must ascribe to the various substances determined quantities of chemical energy. According as the substances arising from a reaction contain more or less energy than the initial materials, energy is taken up or given off. These differences alone come to our knowledge; the absolute values of the chemical energy of each single substance are for us absolutely inaccessible.

Every form of energy may be resolved into two factors, which possess quite definite properties. The one, the factor of intensity, has its definite value for every portion of energy which is specially limited, and the equality of these values in two regions is the condition that on their combination the energy in question is in equilibrium; otherwise it passes from the territory of higher intensity to that of lower.

The second factor I have proposed to call capacity. It measures the quantity of energy which exists in the region in questlon and takes place in a given change of intensity. It in a general property of the magnitudes of capacity

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* From the *Zeitschrift fur Physikalische Chemie.*

that they follow the law of persistence in such a manner that in a defined structure through the boundaries of which energy neither enters nor escapes every magnitude of capacity retains its value unchanged. This proposition, single cases of which have long been known, has been of late advanced in a general form by Le Chatelier; it has an exception conditioned by the phenomena of thermic conduction and radiation, but which does not come into consideration for our further discussion.

What are these magnitudes in chemical energy? The factor of capacity is most easily recognised. The property of being preserved belongs in chemical processes to the quantities of matter, which must consequently be regarded as magnitudes of capacity. The magnitude of the intensity of chemical energy may then be defined as a quotient:—

$$\frac{\text{Energy}}{\text{Capacity.}}$$

It appears therefore as the work corresponding to the transfer of a given quantity of matter from one condition to another, divided by this quantity.

It is therefore not possible to determine values of chemical intensity absolutely, but only the differences of values for two defined conditions are accessible to measurement. It must also be emphasised that in this transfer all other energies must have intensities of constant value.

It will at once appear that the above determination of the value of chemical intensity, or of the chemical potential, as it was named by Villard Gibbs, agrees with the general definition of the magnitudes of intensity if we apply it to the question of equilibrium. Equilibrium presupposes equal intensities; whence it follows that for the unit of the quantity of matter on the transfer from one of the regions of equilibrium into the other, the work consumed or supplied must = O. This is in fact the definition of equilibrium.

After the factor of intensity of chemical energy has thus been recognised, the production of a "chemometer" seems to be merely a practical question like that of the thermometer after the concept of temperature had been decided. But if we seek to carry out the matter practically we encounter a peculiar difficulty which lies in the deficient comparability of chemical magnitudes. Here we must pause in order the better to survey the nature of the question.

Temperatures, masses, and many other magnitudes, are finally determined when we give their commercial value. Two temperatures the values of which (measured in equal units) are the same, are perfectly equal and differ in nothing. This simplicity of determination is met with in all magnitudes. For instance, electric potentials with the same numerical value are not necessarily equal, as they may have different signs (+ or −), and they require two determinations. Velocities, forces, magnitudes of motion, requires still more determinations.

(To be continued).

A NEW HYDROGEN SULPHIDE GENERATOR.

By J. I. D. HINDS.

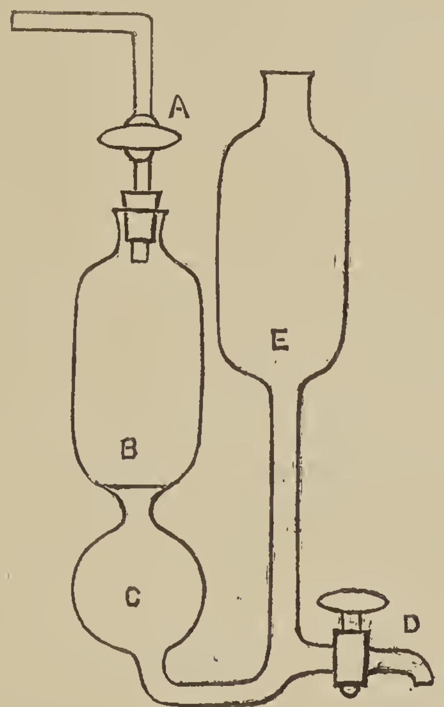
The accompanying figure shows a hydrogen sulphide generator in which objectionable features are reduced to a minimum, and the greatest convenience secured.

At B is a perforated disc of lead, glass, or porcelain, which supports the ferrous sulphide. When the stopcock at A is closed the acid is forced back by the gas into the vessel E. The globe C receives the gas, and prevents it bubbling back into E. When the acid is exhausted it is drawn off at D and a new supply added above.

The advantages of the apparatus are as follows:—

1. It is in one piece.
2. The pressure is small when the cock is closed.
3. The quantity of escaping gas is reduced to a minimum.
4. It is conveniently filled and emptied.
5. It is always ready.

The apparatus is furnished with a suitable support. It may be made of any size. The one now in use in the laboratory of Cumberland University has vessels and globe 8 c.m. in diameter. It was made for me by Messrs. Eimer and Amend, New York, and is giving entire satisfaction.



Cumberland University, Lebanon,
Tenn., U.S.A.

ON COMBUSTIONS.

By THOMAS T. P. BRUCE WARREN.

The determination of carbon and hydrogen in a substance where oxygen is estimated by difference admits of a degree of accuracy which, so far as hydrogen and oxygen are concerned, is simply marvellous, provided that ordinary care in manipulation is used.

In working with hydrocarbons containing sulphur, chlorine, bromine, and iodine, the estimation of hydrogen and carbon is not so satisfactory, nor so simple; we can make sure, with the first class of compounds, that every trace of moisture is removed from the tube and its contents before inserting the platinum boat with the material to be burnt.

Lead chromate cannot be dried in this way: hence moisture and dust, if present, cannot be got rid of; an element of uncertainty may arise if volatile compounds are produced, which sweep over the fused chromate, without being perfectly burnt.

Mixing in a combustion tube, powdered lead chromate with hydrocarbons of the second class by means of a wire is by no means satisfactory; add to this, that when a combustion is finished the tube cannot be used again, and the residual ash of the compound is lost, so that we cannot feel certain that all the carbon has been burnt. By combining the methods used for these two classes of hydrocarbons I obtain a degree of precision with the second class equal to that of the first class, and, what is of equal importance, the tube is left in a condition that it can be used several times without being re-packed.

Some previously ignited asbestos (long fibre) is picked to pieces and well dusted with finely.powdered lead chromate, which is loosely rammed into the tube.

A straight combustion-tube, 800 m.m. long, is packed as follows:—

A good-fitting cork which serves to keep out dust, and allows the materials to be added without the chance of falling out. Asbestos plug, about 80 m.m. long when well rammed down unto the cork. A tightly rolled-up copper-gauze cylinder, 25 m.m. long. Granulated copper oxide, 200 m.m. Copper-gauze cylinder, same as first, which keeps the oxide well together. A loose asbestos plug, 5 m.m. A loosely rolled-up plug of silver-foil, 25 m.m. Asbestos fibre, well dusted with finely-powdered lead chromate, 200 m.m., and which must not be too tightly rammed down. A plug of silver-foil, similar to the first, which prevents anything from falling into the platinum or porcelain boat, which occupies about 10 om.m. Plug of silver-foil, about 100 m.m. A good fitting cork. The corks can be bored when required, and the asbestos plug removed from the front part of the tube, some chemically clean copper turnings being inserted in its place, but only filling about one-half the space.

It is a good plan to keep a few tubes packed ready for use, omitting the boat and last silver plug.

To prepare the packed tube for use, and to make sure that it is not too tightly filled; replace the corks with perforated stoppers, either of cork or rubber; place in the furnace, and aspirate a current of dry air or oxygen, freed from CO_2, through the tube. Light the burners under that portion of the tube containing the copper cylinders and oxide, and, when it is well heated, turn on the other burners under the lead chromate and silver cylinders. The tube may be occasionally turned round, so as to ensure a gradual and uniform heating. After heating for one hour, and the copper oxide is fairly red-hot, the absorption-tubes are attached, after the prepared turnings are placed in the combustion-tubes; the stopcock of the aspirator is now adjusted for a very steady flow of air or oxygen. The joints are tested in the usual way.

The tared boat, containing 0·1 to 0·15 grm., is inserted, and also the following silver plug; the jets are opened under the boat and plug, and the combustion is allowed to proceed slowly.

A little of the substance is previously burnt off in a porcelain crucible, so as to become familiar with the colour and quantity of ash, and also to ascertain whether a platinum or porcelain boat would be preferable to use. Generally the carbon from the second class of compounds is much more difficult to burn than that from the first class. It is best to repeat the combustion until two consecutive results agree fairly well, and, as the same tube can be used over and over again, it is possible to finish four combustions, or even more, in a single day.

The copper turnings in the front part of the tube may be conveniently replaced by a plug of copper-gauze, provided it is left sufficiently bright to break up any oxides of nitrogen. To make sure whether nitrogen compounds are present, a preliminary test is made by fusing with metallic sodium or potassium in a test-tube, and examining the aqueous filtrate for cyanogen.

The same filtrate may be used to supply an approximation as to the sulphur and halogens present.

The mineral portion of the ash is examined in the usual way; it would clearly be wrong to trust only to what is left in the boat, as the volatile hydrocarbons may contain sulphur, halogens, nitrogen, oxygen, or certain metals,—which, of course, are carried away; metals which form volatile oxides, and are not arrested in passing over the lead chromate or copper oxide, will condense on the copper turnings in the front part of the tube, which, in such a case, must not be heated too strongly.

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.*

By AMOS PEASLEE BROWN.

(Continued from p. 132).

Action of 3 per cent Solution of Potassium Permanganate at Ordinary Temperature.

The conditions of this series of experiments were the same as those of the last. The tendency of the results to fluctuate instead of showing a gradual progression is now very marked. One of the one-hour pyrite oxidations shows more sulphur oxidised than is shown by any other individual result of the series. No explanation can be offered for such a discrepancy as this. On the other hand, the high result shown in the three-hour oxidation is quite easily explained by the marcasite having been little, if any, caked in this experiment. The two low results of pyrite three hour and marcasite four-hour oxidations are readily explicable on the ground of caking of the material. As the barium sulphate was often determined several days after the oxidation was completed, it is obvious that no reliable notes could be made concerning the caking or non-caking of the mineral in the permanganate. With this strength of solution it is evident, too, that the main action of the permanganate is complete at the end of one hour, notably in the case of the marcasite, and it is only when very vigorous agitation exposes fresh surfaces of the mineral to the action of the $KMnO_4$ that any further action can take place. We therefore see that marcasite in one hour gives up as much sulphur as in five hours, and this is very graphically shown on Pl. xvii.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 3 per cent Solution of $KMnO_4$ at 22°.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with 3 per cent solution $KMnO_4$ cold	1·65	2·23	2·80	2·47	2·81
	(3·55)	2·31	(1·58)	2·62	2·28
Marcasite with 3 per cent solution $KMnO_4$ cold ..	2·72	2·17	2·87	2·88	2·83
	2·87	2·33	(3·31)	(1·89)	2·77

Action of 5 per cent Solution of Potassium Permanganate at Ordinary Temperature.

In this series, as in the last, the action, as far as pyrite was concerned, was practically complete at the expiration of the first hour, but in the case of the marcasite this point was not reached until probably the end of the second hour, and, in fact, in one case was progressive to the end. But one very great discrepancy is to be noted here in the three-hour column with marcasite. The low result in the next column is explained by caking.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 5 per cent Solution of $KMnO_4$ at 22°.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with 5 per cent solution $KMnO_4$ cold	2·39	3·03	3·22	2·89	2·79
	3·15	3·15	2·32	—	3·24
Marcasite with 5 per cent solution $KMnO_4$ cold ..	2·10	3·06	3·82	3·16	3·39
	2·52	3·76	(5·83)	(2·44)	4·17
			2·77		

This series finishes the experiments at ordinary temperatures. In all of them the action was comparatively slight, not exceeding at most 10 per cent of the contained sulphur in the mineral, which would not be sufficient to show any marked difference between the two minerals as bearing on their constitution, if the constitution which seems to be indicated by subsequent experiments (to be presently described) is the true one.

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* Read before the American Philosophical Society, May 18, 1894.—From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

The oxidations with potassium permanganate at a temperature of 100° were conducted by suspending the vessel containing the mineral and solution in boiling water. Both stoppered bottles and thin glass flasks closed with perforated corks were used for this series of experiments. The water was kept continually boiling, and the bottles or flasks were immersed deep enough to cover that portion of them containing the permanganate. Six or eight oxidations were made at one operation. The permanganate solution, after it had acted the required time, was treated as in the experiments conducted at ordinary temperatures described above. Much more active oxidation took place at this temperature (100°), but the tendency of the mineral to cake together was much more marked, and now this took place with pyrite as well as with marcasite. Moreover, the deposition of manganese dioxide in every case was now very great, causing often a stoppage of the oxidation until it could be dislodged. As these oxidation experiments had already occupied much time, only one trial was now made at each concentration of solution for each hour from one to five, unless, as before, marked discrepancies occurred, when two or more trials were made. The series of results are hence not so regular as they would have been had more trials been made, these irregularities arising from the difficulties that have been mentioned, as well as from the fact that the dilute solutions soon became exhausted, and that all solutions suffered some evaporation, but some more than others, causing irregular strength with the same solution. Nevertheless, the results agree in kind with those obtained at ordinary temperature, but differ widely in degree. Whereas at ordinary temperature the greatest amount of sulphur oxidised in marcasite by the five-hour trial with 5 per cent permanganate was 4·17 per cent, at 100° this became 16·36 per cent, or about four times as much.

Action of $\frac{1}{100}$ Normal Potassium Permanganate Solution at 100°.

The results given in the following Table show perhaps more strongly than either of the other series of experiments at 100° the effect of the different disturbing causes that have been mentioned. It especially shows the effect of caking of the pyrite, which now came in as an important disturbing factor. The result of this caking is shown in the three- and four-hour results with pyrite, both being very low. Marcasite, on the other hand, invariably caked and stuck to the bottom of the bottle, but as this was a constant source of error in this case, the results show a gradual and fairly even increase. Irregular results with marcasite were now largely conditioned by the evaporation of the solution or by the fact of whether the mineral was evenly caked over the inner surface of the vessel or concentrated in spots. The result of this latter way of caking will be better seen in some of the subsequent series of experiments.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a $\frac{1}{100}$ Normal Solution of $KMnO_4$ at 100° C.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with $\frac{1}{100}$ N. $KMnO_4$ at 100° C.	4·05	4·72	3·36	2·04	5·64
Marcasite with $\frac{1}{100}$ N. $KMnO_4$ at 100° C.. ..	3·17	3·84	3·76	5·63	5·61

(To be continued).

Royal Institution.—On Thursday next, March 28th, Dr. E. B. Tylor, F.R.S., will deliver the first of a course of two lectures at the Royal Institution on "Animism as Shown in the Religions of the Lower Races." The Friday Evening Discourse on March 29th will be delivered by Professor H. E. Armstrong, President of the Chemical Society. His subject will be "The Structure of the Sugars, and their Artificial Production."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 7th, 1895.

Dr. Armstrong, President, in the Chair.

Messrs. H. F. Stephenson, E. Joseph, H. L. Robinson, D. B. Butler, F. C. Sharrott, and J. A. Hatfield were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Prosper Henry Marsden, 47, Alma Road, Birkdale; Robert Selby Morrell, M.A., Ph.D., Gonville and Caius College, Cambridge; Frederick Gwilym Trehaine, Llyndirw, Llanishen, near Cardiff; Arthur William Warwick, Minah Mine, Wickes, Montana, U.S.A.

Notice was given of the following alterations in the by-laws proposed by the Council:—

In By-law I., at line 7, after the words "personally known" to strike out the remainder of the paragraph and substitute the following:—

"And the name of such Candidate shall be read at three ordinary scientific meetings, and such Certificate shall be published in full in the Society's *Proceedings*, and suspended in the Society's rooms or place of meeting, until the Candidate has been duly balloted for."

In By-law V., lines 2—4, to substitute the words "be two annual subscriptions in arrears," for the words "have left his subscriptions unpaid for two years, reckoning from the first of January preceding."

Of the following papers those marked * were read:—

*27. "*Dimethylketohexamethylene.*" By F. Stanley Kipping, Ph.D., D.Sc.

The oil obtained on distilling the calcium salt of $\alpha\alpha'$-$\alpha\alpha'$-dimethylpimelic acid with soda-lime (*Proc. Chem. Soc.*, 1892—93, 121—68) has been further investigated; the dimethylketohexamethylene which it contains has been isolated in a state of purity by acting on the fractionated product with hydroxylamine, separating the crystalline oxime thus produced, and decomposing it with hydrochloric acid.

Dimethylketohexamethylene is a colourless, mobile liquid boiling at 174—176°; it readily volatilises with steam, and has a very strong peppermint-like odour.

The oxime, $C_8H_{15}NO$ (found C=68·03, H=10·76; calc. C=68·08, H=10·64 per cent) crystallises from dilute alcohol in long needles melting at 114—115°; it has a strong smell very similar to that of camphor oxime.

When dimethylketohexamethylene is treated with warm, moderately concentrated nitric acid, it is rapidly attacked, but the first product of oxidation was not obtained in a crystalline condition; on prolonged boiling with nitric acid the ketone is converted into a crystalline substance, melting at 65—68°, the properties of which, as far as could be ascertained, are identical with those of the lactone of α-hydroxy-α-methylglutaric acid.

*28. "*The Use of Barium Thiosulphate in Standardising Iodine Solution.*" By R. T. Plimpton, Ph.D., and J. C. Chorley.

The authors find that barium thiosulphate, $BaS_2O_3H_2O$, prepared by precipitation from solutions of sodium thiosulphate and barium chloride, is well adapted to the titration of iodine solutions. The substance can easily be obtained pure, keeps well, and reacts readily with a solution of iodine, while the progress of the reaction is marked by the gradual disappearance of the crystals which are oxidised to soluble barium tetrathionate. An important advantage in the use of barium thiosulphate is its high molecular weight, 267 parts of the substance corresponding to 127 parts of iodine. 50 grms. of sodium thiosulphate and 40 grms. barium chloride are dissolved each in 300 c.c. of water, the warm solutions mixed, and the crystalline powder which soon separates collected, thoroughly washed with cold water, and dried at 30° C.

The precipitate has the composition $BaS_2O_3H_2O$, and would lose water if dried at a much higher temperature.

In performing the titration a weighed quantity of the powder is placed in a stoppered bottle and shaken with water; the iodine is run in until the thiosulphate is almost dissolved, starch solution is then added, and the process completed, care being taken to thoroughly shake the bottle after each addition of iodine.

29. "*The Melting-points of Racemic Modifications and of Optically Active Isomerides.*" By F. Stanley Kipping, Ph.D., D.Sc., and William J. Pope.

The melting-point of a racemic compound is, in almost all cases, different from that of its optically active isomerides; only a few substances are known of which the racemic and optically active isomerides have the same melting-point, and even in these cases it is by no means certain that the supposed racemic modification is not merely a mixture in equal proportions of the two isomerides of opposite optical sign.

During the investigation of π-monobromocamphor, we found the optically inactive form of this substance to be a true racemic compound, since it crystallises in an optically biaxial system, whilst its dextro-isomeride crystallises in the uniaxial tetragonal system; both racemic and active forms have the same melting-point, the two substances melting sharply at 93—94°. A series of determinations of the melting-points of various mixtures of these isomerides was made in order to ascertain the influence exerted on the point of fusion of the one by the other; this led to the somewhat remarkable result that, in spite of the difference in crystalline form, mixtures of the two substances, as well as the pure compounds themselves, melt at the same temperature, viz., 93—94°.

On examining the corresponding chloro-derivatives, we found that dextro-π-monochlorocamphor also melts at the same temperature as its inactive isomeride; further, the melting-point of mixtures of the two substances is always the same as that of the pure constituents. We cannot assert that the inactive modification of π-monochlorocamphor is a true racemic modification with the same certainty as in the case of the bromo-compound, the crystals of the former being very poorly developed and not suitable for crystallographic measurement.

The racemic nature of inactive π-monobromocamphor is, however, beyond all question, and we therefore conclude that it is possible for a true racemic compound not only to melt at the same temperature as its optically active isomeride, but also to have no effect on the melting-point of the latter when mixed with it. This behaviour is analogous to that of mixtures of two isomorphous substances for which the curve plotted between the molecular compositions and the melting-points is a straight line joining the melting-points of the two pure substances.

30. "*Phenyl Ethers of Methylene- and Ethylene-glycols. Synthesis of α-Methylbutyrolactone.*" By E. Haworth, B.Sc., and W. H. Perkin, jun., F.R.S.

These substances, which are required in the course of some synthetical experiments now in progress, were prepared as follows:—

Methyleneglycol diphenylether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}C_6H_5$, is obtained when methylene chloride is digested in alcoholic solution with sodium phenate; it is a colourless, crystalline substance, which melts at 20°, and distils at 205° (50 m.m.).

Ethyleneglycol phenylether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is formed quantitatively when glycolchlorhydrin reacts with sodium phenate; it is a thick, colourless liquid, which boils at 165° (80 m.m.).

When ethylene bromide is digested with sodium phenate, *bromhydrin phenylether*, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2Br$, a colourless, crystalline mass, m. p. 32°, b. p. 144° (40 m.m.), is obtained with glycoldiphenylether,—

$$C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5.$$

colourless crystals, m. p. 96°.

Chlorhydrin phenylether, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$, is obtained when ethylenechlorobromide, $Br{\cdot}CH_2{\cdot}CH_2Cl{\cdot}$, is digested with sodium phenate; it is a colourless, crystalline solid, which melts at 30°, and distils at 220°.

The preparation of α-methylbutyrolactone was conducted as follows:—

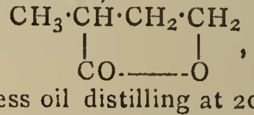
The sodium compound of ethylic methylmalonate was digested in alcoholic solution with bromyhdrin phenylether, and the resulting *ethylic γ-phenoxyethyl-α-methylmalonate*,—

$$(COOC_2H_3)_2{\cdot}C(CH_3){\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5,$$

a colourless liquid, b. p. 230° (45 m.m.), converted by hydrolysis into *γ-phenoxyethyl-α-methylmalonic acid*,—

$$(COOH)_2{\cdot}C(CH_3){\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5.$$

This crystalline acid, which melts at 125°, is decomposed on distillation into carbon dioxide and γ-phenoxyethyl-α-methylacetic acid (m. p. 77°); and this, by treatment with hydrobromic acid and subsequent digestion of the product with sodium carbonate solution, yields phenol and *α-methylbutyrolactone*,—



$$\begin{array}{l} CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_2 \\ \qquad | \qquad\quad | \\ \qquad CO{-}{-}{-}O \end{array},$$

which is a colourless oil distilling at 201°.

31. "*Methyl Isobutyl Acetic Acid*,

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH(CH_3){\cdot}COOH.$$

By W. H. Bentley, B.Sc., and M. W. Burrows, B.Sc.

This acid, which has not hitherto been described, was required for the purpose of comparing its properties with those of some fatty acids obtained by fusing camphoric acid with potash. The present paper deals with its preparation and properties.

Isobutyl bromide, $(CH_3)_2{\cdot}CH{\cdot}CH_2Br$, was heated with the sodium derivative of ethylic methyl malonate, the product being ethylic methylisobutyl malonate,—

$$(CH_3)_2{:}CH{\cdot}CH_2{\cdot}C(CH_3)(COOC_2H_5)_2,$$

distilling at 230—235°. This, on hydrolysis, yielded the corresponding dibasic acid—methylisobutylmalonic acid, $(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}C(CH_3)(COOH)_2$, which melts at 122°, and on distillation is decomposed, forming methylisobutylacetic acid, $(CH_3)_2CH{\cdot}CH_2{\cdot}CH(CH_3){\cdot}COOH$. The pure acid boils at 204—205°, and in its properties resembles the other higher acids of the fatty series.

The following derivatives have been prepared in order to assist in its identification,—

Ethyl Salt, $C_6H_{13}{\cdot}COOC_2H_5$.—A colourless oil boiling at 165—166°.

Anilide, $C_6H_{13}{\cdot}CO{\cdot}NH{\cdot}C_6H_5$.—A colourless solid crystallising from petroleum in silky needles; m. p. 110°.

p-*Toluide*, $C_6H_{13}{\cdot}CO{\cdot}NH{\cdot}C_7H_7$.—A colourless solid melting at 86°.

Anniversary Meeting.

This meeting, at which the election of Officers and Council for the ensuing year will take place, will be held on Wednesday, March 27th, at 3 o'clock in the afternoon.

PHYSICAL SOCIETY.

Ordinary Meeting, March 8th, 1895.

Mr. Walter Baily, Vice-President, in the Chair.

Mr. Naber exhibited and shortly described "*A New Form of Gas Voltameter.*"

The chief advantages claimed for this instrument are that either the oxygen or the hydrogen can be collected separately, and that the level of the liquid inside and outside the burette can be made the same: thus no correction has to be applied to the volume of the gas on this account. Variations in the temperature and barometric pressure are allowed for by reading an air thermometer, which is fixed alongside the burette. The inventor considers that this instrument will compare favourably in accuracy with the copper and silver voltameters now in general use.

Prof. S. P. Thompson considered, that now so much care had been bestowed on the design of a gas voltameter, this instrument might come into more general use than heretofore.

Dr. Johnstone Stoney, F.R.S., exhibited—(1) "*The Local Heliostat*"; (2) "*An Improvement in Siderostats.*"

By a local heliostat the author means one which can only be used in plates the latitudes of which differ slightly from that of the place for which the instrument was specially constructed. The limits within which the instrument works with sufficient accuracy for ordinary spectroscopic work are such that one instrument can be used in any place in the British Isles. The heliostat exhibited was a modification of one previously described by the author, which is now in very general use, and it is capable of sending a reflected ray in any direction in, or nearly in, a horizontal plane. In the new instrument the pendulum clock, previously used to supply the motive power, is replaced by a balance-wheel clock; this change decreases the cost of the instrument, while it adds to its portability. A tangent screw, worked by a long rod, supplies a slow motion for adjusting the position of the reflected beam, and is of use when examining the spectra of the solar prominences, &c. The instrument is adjusted in the meridian by means of a gnomon and horizontal divided circle, which form a sundial. This divided circle is so arranged that it is always horizontal when the polar axis is in adjustment, and can therefore be used whatever the latitude of the station at which the observations are being made. In connection with the use of a heliostat in conjunction with a spectroscope, the author recommends, when using a grating, the introduction of a large glass prism between the heliostat and the slit of the spectrometer. An impure spectrum is thus formed on the slit, and, by moving the slit to the part of this spectrum corresponding to light of the wavelength under observation, the difficulties due to the overlapping of the spectra may be in a great measure overcome. After mentioning that the great difficulty in designing a siderostat which should work with "astronomical accuracy" is to get a form of sliding motion which should be free from back-lash and should move perfectly regularly, Dr. Stoney exhibited a model of a form of mechanism for obtaining such a motion, which he had devised. The principle on which the instrument depends is that, if you have a point fixed to a circle which rolls on the inside of another circle of double the diameter, this point will describe a straight line. The smaller disc does not, in the model exhibited, roll directly on the larger disc, but an idle wheel is introduced which rolls on the *outside* of both the discs. Slip is avoided by placing steel bands between the idle wheel and the discs, one end of each of the two bands being fixed to the circumference of the idle wheel, while the other ends are fixed one to the circumference of each of the disks. Back-lash is prevented by means of a spiral spring attached to a point in the smaller disc, this point being so chosen that it moves nearly perpendicularly to the direction in which the spring acts. Hence the spring is always stretched to nearly the same amount, and no extra strain is brought to bear on the driving clock in different portions of the instrument.

Prof. S. P. Thompson considered that the best method to employ when using sun-light was to incline the telescope, &c., parallel to the polar axis, under which circumstance the mirror of the heliostat need only rotate about a vertical axis.

A paper "*On a Simple Form of Harmonic Analysis*" was read by Mr. G. U. Yule.

At a former meeting of the Society Prof. Henrici showed a form of analyser in which the paper on which the curve is traced was given a to-and-fro movement, a planimeter being used as an integrator. The author, being struck with the advantages of the use of a planimeter both as regards cheapness and simplicity, has devised another form of analyser, in which a planimeter is used. The principle on which this instrument works is as follows: — Suppose we have a straight line (XX) which can move parallel to the base line of the given curve, so that every point in this line describes a perpendicular to the base. Further, suppose that a disc, the circumference of which is some aliquot part of the base of the curve,—say $2\,l/n$ where $2\,l$ is the base length, is capable of rolling on the line (XX) without slip. If the centre of the disc is brouget over the initial point of the curve, and any point (D) at a distance r from the centre on a horizontal diameter is marked; then, if the centre of the disc is made to describe the curve which is to be analysed, the area of the curve described by the point D is given by the equation—

$$R_1 = \alpha + \cos n\,\pi . \frac{r\,n\,\pi}{l} \int_{-l}^{+l} y \sin n\,\theta . d\,x,$$

where α is the area of the curve to be analysed. Similarly, if the point D is taken originally on a vertical diameter, the area of the curve swept out is—

$$R_2 = \alpha + \cos n\,\pi . \frac{r\,n\,\pi}{l} \int_{-l}^{+l} y \cos n\,\theta . d\,x.$$

In any practical case it is convenient to take r some multiple of $1/\pi$ units of length, say 10; then the above equations become—

$$R_1 = \alpha + \cos n\,\pi . 10\,n\,B_n$$

and

$$R_2 = \alpha + \cos n\,\pi . 10\,n\,A_n,$$

where B_n and A_n are the coefficients of $\sin n\,\theta$ and $\cos n$. in the Fourier series expressing the equation to the curveθ The areas of the curves traced out by the point D (R_1 and R_2) are obtained by allowing the tracing-point on an Amsler planimeter to rest in a small conical hole at D. The line XX is the edge of a rolling parallel ruler, which has a rack cut along it. A series of toothed wheels give the coefficients of the different terms in the series. In the instrument exhibited there were wheels to give the first four terms, but the author said it was possible to work with wheels which gave the sixth term. The above analyser was the outcome of a simple step-by-step integrator which the author had devised. In this case the base line of the curve, having been divided into a number of equal parts, then by means of a scale of sines attached to the instrument, the tracing-point of a planimeter is set at a point whose abscissæ is $\sin n\,\theta$, while it is moved parallel to the axis of y through a distance, $\delta\,y$ corresponding to one of the elements into which the base was divided.

Prof. Henrici said he had at one time considered the question of constructing an analyser which should employ a planimeter as the integrator, and he was particularly pleased with the instruments exhibited. Since the area required was the difference between the area of the original curve which is traced out by the centre of the disc (K) and the curve traced out by the point D, and since this area is really the area swept out by the straight line KD, if we attach an integrating wheel to the disc with its axle parallel to KD, the required area can be directly obtained from the reading on this wheel. In addition, if a second integrating wheel were fixed to the disc with its axle perpendicular to KD, the coefficients of $\cos n\,\theta$ and $\sin n\,\theta$ could be both obtained by going round the curve once. The instrument devised by Mr. Yule was practically the inverse of one he (Prof. Henrici) had invented.

Dr. Burton pointed out some incorrect signs in the proof given. These, however, do not affect the final expressions obtained.

Mr. Inwards suggested that errors due to back-lash might be avoided by using either a double wheel or a double rack, so that by means of a spring each side of the teeth which were engaged might be in contact at the same time.

Prof. MINCHIN gave a short account of a paper by Mr. H. N. ALLEN, entitled "*The Energy Movements in the Medium Separating Electrified or Gravitating Particles.*"

The object of the paper is to trace out the equi-potential surfaces and lines of flow for two electrified points or gravitating particles, and then to consider the paths along which the "energy cells" move when the charged points or gravitating particles either move towards or away from one another. By energy cell the author understands the small volume of the dielectric bounded by the walls of a tube of force and by two neighbouring equi-potential surfaces, which can be looked upon as containing a certain definite amount of energy. The author gives two figures showing the paths of the energy cells (1) when the changed particles come together and meet, (2) when they separate and move off to infinity in opposite directions. Using Maxwell's expression for the pressure along the lines of force and the equal tension at right angles required by his theory to account for the attraction exerted by the sun on the earth, the author has calculated the energy density in the medium at the surface of the sun. The value obtained is 16 horse-power hours per c.c. Hence he concludes that at a distance from all gravitating bodies a c.c. of ether contains at least this amount of energy. Prof. Minchin showed how, by the use of polar co-ordinates, the expressions given by the author could be simplified. He also gave a graphical method of obtaining the equi-potential surfaces for any configuration, having given those for any other configuration. He pointed out that by a similar line of reasoning to that used by the author, the energy per c.c. of the medium at the surface of Arcturus must be 8100 times as great as at the surface of the sun, so that the minor limit given above by the author must be multiplied by 8100 at least.

NOTICES OF BOOKS.

A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali, with the Collateral Branches. By GEORGE LUNGE, Ph.D., Professor of Technical Chemistry at the Federal Polytechnic School, Zurich (formerly Manager of the Tyne Alkali Works, South Shields). Second Edition, Revised and Enlarged. Vol. II. London: Gurney and Jackson (Successors to Mr. Van Voorst). Large 8vo., Pp. 930. 1895.

THIS work, in its entirety, may almost be characterised as an encyclopedia of the "heavy" chemical manufactures. The author, in his introduction to the volume now before us, remarks that though the Leblanc process will probably not survive to a remote future, it is still "necessary to describe it, both because it is sure to be carried on for a considerable further period, and because its fundamental operations are typical for alkali-making, and also generally for other branches of chemical industry."

Dr. Lunge begins with an account of the properties and occurrence in nature of the raw materials and products of the alkali industry.

On the occurrence of common salt in nature we find some highly interesting details. The common salt of Cheshire, a district mentioned as the seat of the greatest salt industry in the world, is stated as containing only 98·250 per cent of natural NaCl. Many commercial qualities contain as little as 95 per cent, whilst some of the samples obtained from the Astrachan salt lakes contain as much as 99 per cent. The yearly average home production in Britain exceeds two million tons, and the exportation is now only 700,000 tons. The production in India is given as about one million tons, though in the north-western provinces and in Affghanistan it might be indefinitely increased.

Little as it is now regarded, sodium sulphate occurs in various parts of the world, even in commercial quantities. Near Tiflis there is a bed of very pure Glauber's salt of a thickness of from 5 to 10 feet.

No important natural source of hydrochloric acid is known, which, considering its action on the animal organism, is not to be regretted. The author rightly asserts that factory air should in no case ever contain more than 0·01 per cent HCl. As in the previous line he has stated that "a strong man found air with 0·005 per cent HCl unbearable," we suspect an error in printing, 0·001 per cent seems more likely. It is interesting that of old the three expressions natron, kali, and soda meant the same thing, fixed alkali of any kind. The word "soda" is used by Geber. Hence the Germans have scant justification for retaining the name natron in place of soda. The natural deposits of sodium carbonate—urao, trona—are not unlikely to affect the alkali markets of the world. But where soda occurs in soils, in streams, or lakes in quantities not admitting of collection, it is a serious evil, as being ruinous to vegetation.

The second chapter gives directions for the analysis of the raw materials and the products of the soda industry. The examination of hydrochloric acid is considered at some length, as some possible impurities are much objected to by consumers—a subject to which Dr. Lunge returns elsewhere.

In speaking of the analysis of soda-ash, the author complains that German manufacturers titrate their samples without previous filtration, thus calculating any calcium carbonate as soda. As a standard acid he prefers the hydrochloric to the sulphuric.

As the only indicators needing consideration, he mentions litmus and methyl-orange. Litmus, when properly purified, he considers "hardly less sensitive than methyl-orange." Here we must advise a comparison with Reinitzer's papers on volumetric analysis, a translation of which has appeared in the CHEMICAL NEWS (vol. lxxi., p. 31). Dr. Lunge further gives a caution against the use of tropæolin OO instead of methyl-orange.

The degrees showing the strength or values of soda-ash receive an interesting notice. The English degrees signify the percentage of real or available soda, Na_2O; German degrees show the percentage of sodium carbonate; and French degrees show merely the arbitrary standard of Descroizille.

The French system is very justifiably pronounced the most irrational. The German system quotes as carbonate any other sodium salts which act upon the test acid. Thus they may return a sample of caustic soda as containing 120 per cent or upwards.

The English system was made ridiculous by the conduct of certain analysts acting on behalf of the Liverpool brokers. They insisted on taking the equivalent of soda as = 32 instead of 31, and were thus able to assert that a soda-ash of 50 per cent actual Na_2O should be valued as = 51·6 degrees. Ill fared any work's chemist who refused to make himself a party to this fraud (see CHEMICAL NEWS, vol. xxxii., pp. 267, 280, 302; also xxxiii., 8, 17, 31, 40). The practice was even defended as late as 1884, in *Journal Soc. Chem. Ind.*, pp. 17, 19, 63, 214, 311. Dr. Lunge was even severely attacked for having exposed this absurdity in the first edition of the present work. It was at one time possible to make a good profit by buying soda on the Tyne test and selling it again, nominally at the same price, on the Liverpool test!

The determination of the specific gravity of a soda-ash is of some importance. The denser qualities cost less in freight, and are preferable in all fusings and igniting operations. Sodium sulphate was formerly present in a Leblanc soda as 8 to 10 per cent. Now it is reduced to 0·3 to 1 per cent, whilst in ammonia-soda it may be 0·1 or even less. On the other hand, undecomposed common salt is present in the best Leblanc soda as 0·25 to 0·5 per cent, whilst in the ammonia-sodas it ranges from 0·5 to 2·5 per cent.

Sodium carbonate present in caustic sodas is in some cases not merely useless, but positively injurious. Hence the German trade custom refuses to calculate the carbonate present in caustic as available soda.

Passing over Chapters III., IV., V., VI., not as being as less value, but simply as a question of space, we come to the consideration of the hydrochloric acid produced in the manufacture of salt-cake. At the present day hydrochloric acid no longer counts as a by-product, but is often the main source of profit in the Leblanc process.

The use of lofty chimneys for carrying off the gaseous hydrochloric acid was found to be a very costly failure. A list is here given—on the authority of the Belgian Commission of 1855—showing the comparative sensitiveness of trees to the vapour. The hornbeam is placed as the most sensitive and the grey alder as the most resistant. According to our own observations, the walnut is the most sensitive and the plane the most resistant.

Dr. Lunge does not omit to expose the vulgar error o "smoke consumption." The more completely a ton of coal or coke is consumed the more completely is all its sulphur converted into sulphurous or sulphuric acid. He reminds us that chemical works are often blamed for injury to vegetation which may be chiefly or entirely due to the smoke from domestic chimneys, iron and steel works, &c. He also shows that even at Widnes human health is little affected by hydrochloric acid vapours.

We shall early return to a further notice of this invaluable work.

CORRESPONDENCE.

OERTLING'S BALANCES.

To the Editor of the Chemical News.

Sir,—Kindly note that the balances illustrated in Messrs. Elliott Bros.' Catalogue of January 1st, 1895, are those made by me, though, by inadvertence, in the catalogue Messrs. Elliott Brothers' name appears on the illustrations instead of mine.

Messrs. Elliott Brothers have most courteously undertaken to call attention to this mistake in the copies of the catalogue still in their possession.—I am, &c.,

L. Oertling.

Turnmill Street, London, E.C.,
March 19, 1895.

ARGON.

To the Editor of the Chemical News.

Sir,—I am unaware if the following suggestion has been made, so will ask, Might not argon, this indifferent member of the chemical family, be induced to marry carbon, as nitrogen does when presented to carbon and potash at a red heat? In other words, are argon analogues of KCu and $K_4Fe_2Cy_6$ obtainable?—I am, &c.,

Philip Holland.

London, March 19.

A DISCLAIMER.

To the Editor of the Chemical News.

Sir,—I shall be very greatly obliged if you will allow me to take the earliest opportunity of stating in the Chemical News, as the paper most representative of all the different branches of the chemical profession, that the production appearing in the current number of a journal called *Tit-Bits*, under the title of "A Chemical Analyst and His Work," purporting to be an account of myself and of an interview with me, has been written and published without my knowledge or consent. Its appearance has given me extreme annoyance, and I have addressed to the Editor of the journal a strong representation on the subject (which I hope will appear in the next issue), as well as to the contributor: the latter a friend and past pupil, who, without giving me the faintest hint beforehand of his intention, or asking my permission, has made use of materials gleaned in the course of a purely private conversation, during an ordinary visit from himself, such as he had paid me on several previous occasions.

I should not have dreamed of consenting to the publication of what I regarded as nothing more than confidential chat between two friends. Of course I accept no responsibility for any portion of the account in question; which, moreover, in various respects is distorted and inaccurate.

I thoroughly believe that the contributor's motives were the kindliest; but I have never met with a more forcible example of the application of the saw, "Save me from my friends."

The very first intimation I received that such an article had been written was in a letter from my friend on the morning after the paper was issued from the press.—I am, &c.,

E. Godwin Clayton.

43 and 44, Holborn Viaduct, E.C.,
March 16, 1894.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 9, March 4, 1895.

Notice of the Life and Work of Admiral Paris (of the Section of Geography and Navigation).—E. Guyon.—This extensive memoir contains nothing which can be noticed in the Chemical News, though we must appreciate the tact with which M. Guyon avoids political allusions.

Prophylactic Treatment of Swamp Fevers.—M. d'Abbadie.—The author, on the faith of experience, recommends a daily fumigation of the naked body with sulphur as a preservative against the intermittent or pernicious fevers of tropical climates. (The agent, of course, will not be sulphurous acid, but sulphur volatilised in its free state).

The Month of February at the Observatory of the Parc Saint Maur.—E. Renou.—To find as low a mean temperature for February we have to go back to 1740 and consult the observations made by Réaumur.

Oxides and Sulphides with Acid and Basic Functions. Zinc Sulphide.—A. Villiers.—This paper will be inserted in full.

Calorimetric Researches on Saline Solutions. Sodium Acetate.—E. Morney.—The author represents his results by a curve taking as abscissæ the concentrations and as ordinates the heats of dilution. The curve constructed at 15 is almost rectilinear from the concentration 0 to 10 and ascends rapidly. Then there appears a very decided curvature between the concentrations 5 and 17·5. Above this latter concentration the curve tends to become asymptotic to a right line parallel to the axis of the abscissæ the ordinate of which will be nearly equal to 18.

On Hexamethylene-Amine; Salts of Ammonium; Action of Acids; Production of Primary Amines.—M. Delépine.—This paper does not admit of useful abridgment, and can scarcely merit insertion in full.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xi.-xii., No. 23, 1894.

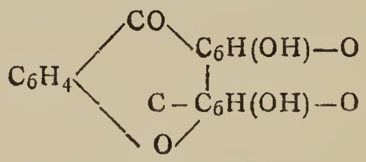
Researches on the Basic Nitrates.—M. Athanasesco.—It is known that the solutions of a great number of basic sulphates if heated in sealed tubes to temperatures varying according to the character of the metal give rise to a basic sulphate more or less crystalline. The author has applied the same process to other metals, and has obtained a basic copper nitrate of the composition $NO_3.H,2CuO,3H_2O$.

Method of Preparing Paraquinones by means of Indophenols.—The author pulverises finely 10 grms. of the indophenol corresponding to the quinone to be obtained. He places the powder in a flask with a long neck, pours in 50 grms. of water, agitates, and drops in gradually 20 grms. pure sulphuric acid. The flask is closed with a stopper having a slight notch at the side, and shaken up again. The reaction is quickly effected. The liquid is then allowed to cool and exhausted with ether. The ethereal solution is transferred to a 1-litre flask, and evaporated by means of a current of air. After the evaporation of the ether, the flask is connected, on the one hand, with a refrigerator and a cooled receiver, and on the other with a flask giving off watery vapour. The steam carries off the quinone, which is found pure in the receiver.

On a New Quinone. Ethylbenzoquinone.—H. P. Bayrac.—The new compound takes the form of brilliant laminæ of a gold-yellow, or, on crystallisation from ether, of long prismatic needles. It has a powerful irritating odour. It melts at 38·2°, dissolves very sparingly in cold water, much more readily in hot water; it is very soluble in ether, but slightly less so in alcohol. It contains—Carbon, 70·33; hydrogen, 5·78; Oxygen, 23·89 per cent.

On a Series of Indophenols. General Method of Preparation.—H. P. Bayrac.—Already inserted.

Constitution of Ceruleine.—Maurice Prudhomme.—Ceruleine contains two hydroxyls, and its constitution may be represented as follows:—



Quinine Chlorhydrosulphate.—Charles Lepierre.—This salt is destined to play a great part in therapeutics, especially for hypodermic injections.

Determination of the Total Nitrogen in Urine by Henninger's Method.—H. P. Bayrac.—A dispute concerning a modification of the Kjeldahl method, which in reality was introduced in 1884 by Henninger, and not, as Moreigne supposes, by Petit and Monfet.

Royal Institution.—The following are the Lecture Arrangements after Easter:—Professor George Forbes, three lectures on "Alternating and Interrupted Electric Currents"; Professor E. Ray Lankester, four lectures on "Thirty Years Progress in Biological Science"; Professor Dewar, four lectures on "The Liquefaction of Gases"; Dr. William Huggins, three lectures on "The Instruments and Methods of Spectroscopic Astronomy" (the Tyndall Lectures); Mr. Arnold Dolmetsch, three lectures on "Music and Musical Instruments of the Sixteenth, Seventeenth, and Eighteenth Centuries"—(1) English, (2) French, (3) Italian (with Illustrations upon Original Instruments); Mr. Seymour Lucas, two lectures on "Picture Making"; Professor Edward Dowden, two lectures on "Elizabethian Literature"—(1) The Pastoral, (2) The Masque. The Friday Evening Meetings will be resumed on April 26th, when a Discourse will be given by Dr. John Hopkinson, on "The Effects of Electric Currents in Iron on its Magnetisation; succeeding Discourses will probably be given by The Earl of Rosse, Veterinary Captain Frederick Smith, The Hon. G. N. Curzon, M.P., Professor Walter Raleigh, Mr. J. Viriamu Jones, Professor Alfred Cornu, and other gentlemen.

MEETINGS FOR THE WEEK.

Monday, 25th.—Society of Arts, 4. (Cantor Lectures). "Commercial Fibres," by Dr. D. Morris.
— Medical, 7.

Tuesday, 26th.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
— Institute of Civil Engineers, 8.

Wednesday, 27th.—Society of Arts, 8. "Modern Photogravure Methods," by Horace Wilmer.
— British Astronomical Association, 5.
— Chemical, 3. Anniversary Meeting. Anniversary Dinner, Hotel Metropole, 7.

Thursday, 28th.—Society of Arts, 4.30. "Chitral and the States of the Hindu Kash," by Capt. F. E. Younghusband.
— Institute of Electrical Engineers, 8.
— Royal Institution, 3. "Animism, as shown in the Religions of the Lower Races," by E. B. Tylor, F.R.S.

Friday, 29th.—Royal Institution, 9. "The Structure of the Sugars and their Artificial Production," by Prof. H. E. Armstrong, F.R.S.

Saturday, 30th.—Royal Institution, 3. "Waves and Vibrations," by Lord Rayleigh, F.R.S.

THE CHEMICAL NEWS.
Vol. LXXI., No. 1844.

DISCOVERY OF HELIUM.*

By Prof. W. RAMSAY, F.R.S.

In seeking a clue to compounds of argon I was led to repeat experiments of Hillebrand on clèveite, which, as is known, when boiled with weak sulphuric acid, gives off a gas hitherto supposed to be nitrogen. This gas proved to be almost free from nitrogen; its spectrum in a Plücker's tube showed all the prominent argon lines, and, in addition, a brilliant line close to, but not coinciding with, the D lines of sodium. There are, moreover, a number of other lines, of which one in the green-blue is especially prominent. Atmospheric argon shows, besides, three lines in the violet which are not to be seen, or, if present, are excessively feeble, in the spectrum of the gas from clèveite. This suggests that atmospheric argon contains, besides argon, some other gas which has as yet not been separated, and which may possibly account for the anomalous position of argon in its numerical relations with other elements.

Not having a spectroscope with which accurate measurements can be made, I sent a tube of the gas to Mr. Crookes, who has identified the yellow line with that of the solar element to which the name "helium" has been given. He has kindly undertaken to make an exhaustive study of its spectrum.

I have obtained a considerable quantity of this mixture, and hope soon to be able to report concerning its properties. A determination of its density promises to be of great interest.

THE SPECTRUM OF THE GAS FROM CLÈVEITE.†

By WILLIAM CROOKES, F.R.S.

By the kindness of Professor Ramsay I have been enabled to examine spectroscopically two Plücker tubes filled with some of the gas obtained from the rare mineral clèveite.‡ The nitrogen had been removed by "sparking." On looking at the spectrum, by far the most prominent line was seen to be a brilliant yellow one apparently occupying the position of the sodium lines. Examination with high powers showed, however, that the line remained rigorously single when the sodium lines would be widely separated. On throwing sodium light into the spectroscope simultaneously with that from the new gas, the spectrum of the latter was seen to consist almost entirely of a bright yellow line, a little to the more refrangible side of the sodium lines, and separated from them by a space a little wider than twice that separating the two sodium components from one another. It appeared as bright and as sharp as D_1 and D_2. Careful measurements gave its wave-length 587·45; the wave-lengths of the sodium lines being, D_1 589·51, and D_2 588·91. The differences are therefore—

	Wave-lengths.	Differences.
D_1	589·51	
		0·60
D_2	588·91	
		1·46
New line.. ..	587·45	

The spectrum of the gas is, therefore, that of the hypothetical element helium, or D_3, the wave-length of which is given by Angstrom as 587·49, and by Cornu as 587·46.

Besides the helium line, traces of the more prominent lines of argon were seen.

Comparing the visible spectrum of the new gas with the band and line spectrum of nitrogen, they are almost identical at the red and blue end, but there is a broad space in the green where they differ entirely. The helium tube shows lines in the following positions:—

		Wave-length.		
(*a*)	D_3, yellow	587·45	Very strong.	Sharp.
(*b*)	Yellowish green ..	568·05	Faint.	Sharp.
(*c*)	Yellowish green ..	566·41	Very faint.	Sharp.
(*d*)	Green	516·12	Faint.	Sharp.
(*e*)	Greenish blue	500·81	Faint.	Sharp.
(*f*)	Blue	480·63	Faint.	Sharp.

I have taken photographs of the spectrum given by the helium tube. At first glance the ultra-violet part of the spectrum looks like the band spectrum of nitrogen, but closer examination shows considerable differences. Some of the lines and bands in the nitrogen spectrum are absent in that from the helium tube, whilst there are many fine lines in the latter which are absent in nitrogen. Accurate measurements of these lines are being taken.

ATTEMPTS TO MAKE ARGON ENTER INTO CHEMICAL COMBINATION.*

By M. BERTHELOT.

Towards the end of the month of February I received from Dr. W. Ramsay some argon contained in a tube arranged for spectrum analysis, and in a small bulb or cylinder sealed at each end before the blowpipe. Dr. Ramsay at the same time wrote me a letter, in which he kindly gave the following information:—The gas "had been circulated in the apparatus for the absorption of nitrogen, until the nitrogen bands disappeared and there was no more contraction. The density of the specimen was 19·95, hydrogen being 1, and the relation between the specific heats 1·64."

It has been with this specimen, guaranteed by Dr. Ramsay, that I have made the following experiments. The gas in the cylinder was removed by immersing it in a vessel of mercury, breaking off the two ends successively, and collecting the gas directly in a small pipette. Its volume was 37 c.c.

The idea which prompted my experiments is the following:—I endeavoured to bring about the combination of argon with other elements under the influence of the silent electric discharge. This discharge is, indeed, much more effectual than the spark, because it more effectually secures the permanence of instable compounds; the effect of the silent discharge being too rapid to cause the subsequent destruction of the products owing to a sensible duration of a high temperature, a circumstance which is opposite in the case of the spark. Nitrogen, for instance, in the presence of hydrocarbon gases or vapours gives rise to most varied products of condensation under the influence of the silent discharge—products which decompose with elevation of temperature; whilst under the influence of the spark only one compound, hydrocyanic acid, is formed, and were this compound not stable at a high temperature nothing would be formed. Carbonic oxide condenses under the influence of the silent discharge, whilst it is almost unaltered by the spark. Again, the silent discharge, acting on a mixture of nitrogen and hydrogen, can produce several percentages of ammonia, while the spark only gives infinitesimal quan-

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* A Paper communicated to the Chemical Society at their Anniversary Meeting, March 27, 1895.

† A Paper communicated to the Chemical Society at their Anniversary Meeting, March 27, 1895.

‡ Clèveite is a variety of uraninite, chiefly a uranate of uranyle, lead, and the rare earths. It contains about 13 per cent of the rare earths, and about 2·5 per cent of a gas said to be nitrogen.

* *Comptes Rendus*, cxx., No. 11, p. 581, March 18, 1895.

tities. Under the influence of the silent discharge, nitrogen is absorbed by water, with formation of nitrite of ammonia, a compound which is decomposed on standing, and spontaneously at the ordinary temperature.

It was therefore necessary to study the action of the silent discharge on the combination of argon with oxygen, hydrogen, and the hydrocarbons. As the quantity of gas at my disposal was small, I tried first the hydrocarbons which lend themselves better to this form of experiment.

I exposed argon to the action of the silent discharge under the conditions described in my "Essai de Mechanique Chimique" (t. ii., pp. 362, 363), which are those of the silent discharge with variable potential, regulated by Ruhmkorff's apparatus, with a vibrating conductor and high tension. The apparatus employed is described and figured in the *Annales de Chimie et de Physique*, 5e serie, t. x., pp. 79, 76, 77, figs. 5, 2, and 3 (1877). It allows removals and accurate measurements. It was under such conditions that I succeeded in causing free nitrogen to be rapidly absorbed hy hydrocarbons, hydrates of carbon, and the most diverse organic matters ("Essai de Mechanique Chimique," t. ii., p. 384).

Argon appears to be equally absorbed, as I shall explain, although with more difficulty. I have especially worked in the presence of vapour of benzene, which is very effective in the case of nitrogen. The action of the silent discharge on the mixture is accompanied with a faint violet glow, visible in darkness. On one occasion, out of five experiments, there was formed at the end of some time a fluorescent body, which gave out a magnificent greenish light and a special spectrum; but the quantities of matter at my disposal were too small to allow me to seek for the conditions necessary to produce these effects.

These are the data of a careful experiment, effected on 10 c.c. of argon. One hundred volumes of gas from Dr. Ramsay were measured, put into contact with some drops of benzene—this increased the volume of the gas about one-twentieth,—and then introduced into the discharge-tube, into which a trace of liquid had entered. The electricity was then allowed to act, with relatively moderate tensions, for ten hours. The total gaseous volume was reduced about a tenth. The vapour of benzene was absorbed by a drop of concentrated sulphuric acid, with the usual precautions, and the volume of the residue was measured; it was reduced to 89 volumes, showing 11 per cent of diminution.

This volume was again mixed with benzene vapour, and the experiment was re-commenced, employing much higher tensions; the volume diminished rapidly. At the end of three hours, all corrections being made, the volume was only 64; that is to say, it had experienced a fresh reduction of 25 per cent.

What remained was again mixed with benzene and submitted a third time to the silent discharge, using strong tensions, for several hours. There was then found a crude gaseous residue measuring 32 volumes after making all corrections. But this residue was not pure argon; it contained nearly half of combustible gases, products of the reaction of the discharge on the benzene. According to eudiometric analysis, these 32 volumes contained—

Hydrogen	13·5
Benzene vapour	1·5
Argon	17·0

It contained no alkaline vapour.

To sum up, of 100 volumes of argon, benzene successively condensed 83 in the state of chemical combination produced by the silent discharge; that is to say, five-sixths. The dimensions of my apparatus would not allow me to go beyond that.

The products of this combination represent too small a weight to permit of a detailed examination. I will only say that they resemble those produced by the silent discharge acting on nitrogen mixed with the vapour of benzene; that is to say, they consist of a yellow, resinous, odorous matter condensed on the surface of the two glass tubes between which the electric action is exerted. This substance, submitted to the action of heat, decomposes, forming volatile products, and leaving a bulky carbonaceous residue. The volatile products of decomposition turn litmus paper blue; this indicates that an alkali is formed in the decomposition. But it was not possible to examine it more closely for want of material. In any case, the conditions under which argon is condensed by hydrocarbons tend to assimilate it still closer to nitrogen.

Let me here observe that if it is permitted to raise the molecular weight of argon to 42 instead of 40—an increase which the limits of error in the experiments hitherto made, in which numbers as high as 51·2 have been obtained, do not entirely exclude—this weight would represent one and a half times that of nitrogen; that is to say, argon would bear to nitrogen the same proportion that ozone does to ordinary oxygen,[*] with this fundamental difference, that argon and nitrogen are not transformable the one into the other; not otherwise than the isomeric or polymeric metals. But I do not wish to insist on such conjectural correspondences.

In any case, the inactivity of argon ceases under the circumstances I have described. When more considerable quantities of argon are available, it will doubtless be easy by the ordinary methods of chemists to take these first combinations or any other analogous ones realisable with oxygen, hydrogen, or water as the starting-point of transformations, and to obtain the normal series of more simple compounds. There is also room for the search for the presence of compounds of argon in organised beings.

CRYSTALLISED CARBON DIOXIDE.[†]

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

When solid carbon dioxide is examined under the microscope, it presents along its edges projecting wire-like crystals which have branching filaments issuing from them apparently at right angles, resembling somewhat the groups of minute crystals seen in crystallised iron, gold, and ammonium chloride.

The rapidity with which the carbon dioxide evaporates makes it difficult to catch the form of the crystals, either by photography or other means.

COMBUSTIONS WITH LEAD CHROMATE.

By THOMAS T. P. BRUCE WARREN.

In packing a combustion tube with copper oxide and lead chromate, as given in a previous communication (Chem. News, lxxi., p. 144), I recommended to insert an asbestos plug between the second copper gauze prism and the first silver foil prism, with the view of preventing any dust of copper oxide reaching the lead chromate. I have since found that by repeated handling some copper oxide gets to the chromate, and in time a little copper chloride is formed, and although the silver prism arrests it, there is just the chance that some may be carried over to the absorption tubes.

If much chlorine is present, it is preferable to omit the copper oxide and to replace it with lead chromate dusted on asbestos.

To make sure that every trace of moisture is removed, heat the tube and asbestos to redness, attach the absorption tubes and aspirate a gentle current of dry oxygen or

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[*] Or, better still, the proportion which the camphenes, $C_{10}H_{16}$, bear to the sesquiterebenes, $C_{15}H_{24}$.

[†] Read before the Aust. Assoc. for the Advancement of Science, Brisbane, January, 1895.

air freed from CO_2 for about one hour; if the weight is unaltered, allow the tube to cool down, insert the boat and substance, and proceed with the combustion.

SYNTHETIC EXPERIMENTS IN THE PYRAZOL SERIES.*

Part I.

By R. von ROTHENBURG.

(Continued from p. 142).

Pyrazolon-(3)-carbonic acid-(4)-orthobenzoïc acid is formed like the foregoing if orthodiazobenzoïc acid is used in place of the diazobenzene salts. It has more decided acid properties, and is distinguished from the former by its greater solubility. It crystallises from dilute alcohol in red needles. Melting-point 227°.

Pyrazolon - (3) - carbonic methylester.—Obtained from hydrazin hydrate and oxalaceticmethylester. It forms yellow crystals, fusible at 226·5—227·5°. Its composition is $C_5H_6N_2O_3$.

(4)-Benzalpyrazolon-(3)-carbonic methylester is obtained from the ester by heating with equimolecular quantities of benzaldehyd to 120—130°. Sparingly soluble in all solvents; forming a yellowish brown powder, which undergoes no change up to 250°.

(4)-Isonitrosopyrazolon-(3)-carbonic methylester.—This compound dissolves in alcohol, glacial acetic acid, and alkalis with a deep red colour, but in ammonia with a violet-blue. It separates from dilute alcohol or acetic acid in yellowish red warty crystals melting at 199—201°, and has rather strongly acid properties.

Pyrazolon-(3)-carbonic ethylester is formed from oxalic-acetic or acetylendicarbonic diethylester by adding gradually hydrazin hydrate to oxalacetic ester, diluted with 4 or 5 parts of alcohol, when heat is liberated spontaneously. It is then heated to ebullition for thirty minutes, and allowed to cool, when the entire quantity of pyrazolon-(3)-carbonyl hydrazin, insoluble in alcohol, is separated out. The alcohol is distilled off, and poured hot into a capsule; the mass congeals; it is drained, washed in ether, and crystallised from ether-alcohol in flat needles; it is soluble in alcohol, almost without limit, sparingly soluble in benzene and ether, freely in methylic and amylic alcohol. It melts at 179°. Its composition is $C_6H_8N_2O_3$.

(4)-Benzalpyrazolon-(3)-carbonic ester is a reddish yellow granular powder sparingly soluble in all solvents, and having the composition $C_{13}H_{12}N_2O_2$.

(4)-Isonitrosopyrazolon-(3) carbonic ethylester is obtained by passing gaseous nitrous acid into the alcoholic solution of the ester. It is easily soluble in organic solvents, and dissolves in alkalis with a deep red, but in ammonia with a violet-blue. From alcohol it crystallises in yellow, acid, granular crystals, fusible at 182°, and of the composition $C_6H_7N_3O_4$.

(4)-Azobenzenepyrazolon-(3)-carbonic ethylester consists of $C_{12}H_{12}N_4O_3$.

Pyrazolon-(3)-carbonic ethylester (4)-ortho-azobenzoïc acid crystallises from alcohol in fiery red needles, fusible at 255°.

Pyrazolon-(3)-carbonamid.—Best obtained from methyl ester and concentrated alcoholic ammonia on heating in a tube to 100—120°. Sparingly soluble in ordinary solvents, and crystallises from water in granular masses; fusible at 219° with decomposition. Well-crystallised derivatives are also obtained from aniline, toluidine, anisidine, phenetidine, naphthylamine, and phenylhydrazine.

Pyrazolon-(3)-carbonylhydrazin has the composition $C_4H_6N_4O_2$. Sparingly soluble in all organic solvents. Crystallises from water in flat needles, fusible at 238—239°.

Pyrazolon-(3)-carbonyl-benzalhydrazin crystallises in fine needles associated in flocks, and decomposed above 250°.

(4)-Benzalpyrazolon-(3)-carbonal-benzyl-hydrazin.—A yellowish red powder, very sparingly soluble in all ordinary solvents, and unchanged at 250°.

(4)-Hydropyrazolon-(3)-carbonyl-hydrazin. If hydrazin-hydrate in excess is allowed to act upon an alcoholic solution of (4)-isonitroso-pyrazolon-(3)-carbon ester, this compound separates as a fiery red precipitate, very sparingly soluble. It is very interesting, since it dissolves with a red colour in alkalis, like the azo derivatives of diazo-salts, and displays on reduction the properties of a true diazo-compound. It dissolves in acids with a yellow-red colour, and is unchanged at 250°.

(4)- Benzalazipyrazolon (3)-carbonyl - benzal - hydrazin proves that the hydrazonhydrazid has retained its nature as a hydrazin derivative. On shaking with benzaldehyd suspended in water the fiery red compound passes into a lemon-yellow derivative, melting at 217·5°.

Pyrazolon-(3)-aldehyd.—A yellow oil, easily re-converted by oxidation into the carbon-acid.

(3)-Dipyrazolonketon is contained in the less volatile fractions of the distillation of pyrazon-carbon acid with lime. It passes over at 202—203°, and shows the characteristic pyrazolon reactions. Its composition is $C_7H_6N_4O_2$.

(3)-Diparazolon-methylenphenylhydrazin is obtained on heating the alcoholic solution of the ketone with phenylhydrazin. It gives the characteristic reactions of the pyrazolones, dissolves readily in organic media, and separates from alcohol in flocks; fusible at 113°.

(To be continued).

EXPERIMENTS ON THE SPONTANEOUS HEATING OF FATTY OILS DIFFUSED IN FIBROUS OR POROUS SUBSTANCES.

By Dr. RICH. KISSLING.

The author had the opportunity of studying a case of spontaneous combustion which was checked at its outset. A cask of boiled linseed oil in a warehouse had been leaking on the previous day, and the leakage had been absorbed in sawdust. This sawdust was put in an iron pail, and left in the warehouse all night. About midnight the watchman observed an empyreumatic odour, and saw a slight smoke rising from the pail, which became a flame, when the pail with its contents was carried into the open air. The fire was quenched before the contents had been too much altered by the heat. There can be no doubt that the ignition was spontaneous. The warehouse was lighted electrically, and no matches were ever introduced.

On a careful experimental examination it was found that on passing a current of dry air through raw linseed oil (previously heated to 100°), it gained daily 0·87 per cent of its weight of the absorption of oxygen. The total increase of weight was 0·41 per cent, and there had been a loss of 0·46 per cent from the escape of volatile matter—acids of the methane series.

If the surface of contact between the fatty oils and the air, and if external refrigeration is prevented, a considerable rise of heat is produced by the process of oxidation, which under favourable circumstances may extend to an actual ignition of the fibrous matter.

The quantity of heat liberated by the spontaneous oxidation of the oil depends:—(*a*) on the chemical nature of the oil concerned, *i. e.*, on its affinity for oxygen; (*b*) on the size of the surface of contact between the oil and the air, *i. e.*, on the mechanical texture of the fibrous or other porous matter, as well as on the relative proportion of

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* From the *Journal Praktische Chemie.*

the oil and such fibrous matter; (*c*) on protection against external refrigeration; and (*d*) on the action of light.

On these conditions it may be remarked, under (*a*), that the behaviour of different oils varies greatly; with rape oil the rise of temperature was not recognisable; with cotton oil it was very trifling; with raw linseed oil stronger; and with boiled oil very considerable. The fibrous substances examined (*b*) differed likewise. The greatest liberation of heat took place with silk fibres; then followed wool, cotton, jute, and lastly hemp. (*c*). The protection against refrigeration is of importance, as the tendency of oils to become oxidised with a liberation of heat rises with the temperature. (*d*) The action of light is similar to that of heat.

The activity of micro-organisms in these processes of oxidation is unimportant.—*Zeitschrift Angewandte Chem.*, Jan. 15, 1895.

(Dr. Kissling omits to state whether the silk fibre used in his experiments was pure or "loaded." The latter article has occasioned serious fires).

THE CHEMOMETER.*

By W. OSTWALD.

(Continued from p. 143).

Such simplicity of determination is not common to all magnitudes. Electric potentials, *e.g.*, are not necessarily equal when their numerical values are alike, as they may have a different sign; they therefore require two determinations. Velocities, forces, quantities of motion, require still more determinations.

Two forces, numerically equal, may differ in sign and in direction, and to determine the direction we require the three cosines of direction in reference to any given system of axes. But all these magnitudes have always a finite number of determining elements by means of which they may be respectively converted.

But the factors of chemical energy are even devoid of this mutual relation. They differ from each other in infinitely many respects. Thus oxygen and iron have no direct relation to each other. We have no means of converting one *grm.* of iron into so and so many grms. of oxygen, or of replacing it by oxygen of an equal value, whilst the values which we have just considered may always be transformed into others of the same kind. And what relates to the capacities of chemical energy must necessarily hold good for the intensities, as the latter are defined by the former.

The only kind of relations which is possible among the chemical factors of energy is expressed by the equations of chemical reaction. When we write—

Iron + Oxygen = Iron Oxide,

we say that there exists between iron and oxygen no direct or mutual relation of conversion; but there exists a relation between the three substances, iron, oxygen, and iron oxide, such that the third can be made from the two former, and, inversely, that iron and oxygen can be produced from iron oxide. The customary expression, that iron oxide *consists* of iron and oxygen, is brief but inaccurate. For in iron oxide we find neither the properties of iron nor those of oxygen; and if we say that, though the attributes of both substances disappear they are still substantially present, we only need to attempt to connect clear and definite conceptions with this expression; the result will be infallibly such that we desist from any further attempt in this direction. Indeed the chemist of the present day becomes so early familiar with the atomic hypothesis (certainly very convenient as a means of instruction) that no doubt suggests itself to him as to the reality of the atoms and their continued existence in compounds. But in an enquiry of a general character it becomes so much the more necessary to separate carefully matter of fact from what is merely hypothetical, in order to have solid ground for our superstructures.

From these considerations we infer that the capacities of chemical energy do not possess, like all other capacities, a common measure, but that they can be reduced to so many mutually independent kinds as there exist so-called elements. Between these elements there exists a relation only in so far that many of them can act upon each other in such a manner that there may arise new substances, and consequently new capacities, which, however, are no longer independent, but have such a relation to the elements that they may be regarded as the sum of the latter. These relations are further subject to the known stœchiometric laws, that of constant proportions, of multiple proportions, and of combining weights. In addition, there is the above-mentioned law of the maintenance of the species, according to which a transition from one element to another is impossible.

The corresponding intensities of chemical energy are subject to exactly the same limitations. Hence, also, there are about seventy kinds which cannot in any manner be referred to each other, and the existing relations between the elements and the chemical compounds obey the stœchiometrical laws.

If we therefore suppose a "chemometer" really executed in manner above mentioned, we cannot be satisfied with a single instrument. We must have at least seventy such appliances independent of each other, one for each element, and should have no means of comparing the indications of the oxygen chemometer with those of the apparatus for hydrogen.

According to these considerations the especial characteristics of chemical energy seem entirely to cut off the possibility of producing such apparatus of a general character. For manometers, electrometers, thermometers, are possible only because all pressures, electric potentials, temperatures, &c., are alike in their nature and the relation of any two individual values of this kind can be fully expressed by a number.

On further reflection, however, the matter does not appear hopeless. Certainly an absolute, universal chemometer is not possible. Still for many cases the intensity of chemical energy may be expressed in a comparable measure, independent of the factors of chemical energy display, in reference to each other, this great number of irreducible cases. This may be effected by the employment of such kinds of energy as are inseparably connected with chemical processes, and the most suitable energy for this purpose seems to be the electrical.

According to Faraday's law, the far-reaching significance of which has only become manifest in our days, in many chemical reactions, especially those in which electrolytes are concerned, there are manifested electrical processes which are proportional to the chemical reactions and are inseparably connected with them. The connection is such that the capacities of electrical energy, the quantities of electricity, are proportional to the capacities of the chemical energy, the quantities of substance, and in different substances the quantity of electricity combined with quantities chemically equivalent, is always the same.

(To be continued).

Rotatory Power of Isomeric Ethers in the Amylic Series.—Ph. A. Guye.—From the author's polariscopic experiments, executed under conditions as comparable as possible, it results that among the amylic derivatives the propyl group is more active than the isopropyl group, and the latter, again, more than the butyl group.—*Bull. de la Soc. Chim. de Paris*, xi.-xii., No. 23.

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* From the *Zeitschrift fur Physikalische Chemie.*

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.*

By AMOS PEASLEE BROWN.

(Continued from p. 132).

Action of 1 *per cent Potassium Permanganate Solution at* 100°.

THE results of the oxidation shown in this series are chiefly remarkable as still further illustrating the action of the solution on the caked material, as shown in the four- and five-hour trials with pyrite and the four-hour trial with marcasite. This latter shows, too, the effect of having the caked mineral massed in one spot. With this exception, the marcasite oxidations are progressive and fairly uniform (the two-hour trial falls somewhat below what it doubtless should be), but the pyrite shows a sharp fall in the four- and five-hour trials. The cause of this has been indicated. That the concentration of the solution by evaporation caused an increase in the action seems to be indicated by the result of the five-hour marcasite oxidation, but this is much more strongly marked in the 5 per cent series in the case of pyrite, which will be referred to later on.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 1 *per cent Solution of* $KMnO_4$ *at* 100°.

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with 1 p. c. $KMnO_4$ at 100° C.	6·03	6·98	8·38	6·11	6·88
Marcasite with 1 per cent $KMnO_4$ at 100° C. ..	6·43	5·61 6·25	8·56	7·40	9·10

Action of 3 *per cent Solution of Potassium Permanganate at* 100° *C.*

The average results of this series of oxidations were very good, with the exception of two members of the series—the marcasite five-hour trial and the pyrite three-hour. This latter was repeated, but with a similar low result. Leaving these two out of account, the average results show a very fairly even rate of progression, which have been brought out in the diagram (Pl. xvii.). It is evident from an inspection of the following table that the marcasite oxidations of the four- and five-hour trials were arrested by some disturbing influence.

Table Showing the Relativc Oxidation of Sulphur in Pyrite and Marcasite by a 3 *per cent Solution of* $KMnO_4$ *at* 100° *C.*

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.
Pyrite with 3 p. c. $KMnO_4$ at 100° C.	5·52 (7·01)	5·77 7·89	6·81 5·16	10·73	11·08
Marcasite with 3 per cent $KMnO_4$ at 100° C. ..	5·25 5·50 (8·67)	7·97	9·42	9·80	7·55

Action of a 5 *per cent Potassium Permanganate Solution at* 100° C.

This series was decidedly the most satisfactory of the experiments conducted at 100°, and, with the exception of the two-hour oxidations, in case of each mineral shows a remarkably regular increase in the oxidation of the sulphur. It illustrates, too, in the case of the pyrite, the effect of the concentration of the solution due to evaporation. This causes a more rapid rise in the results after three hours' action, and notably between four and five hours. This rise is not so well seen from the table as from the plot of the results given in Pl. xvii. Here this rising of the curve after three hours is very marked as contrasted with the curve of the marcasite oxidations.

Table Showing the Relative Oxidation of Sulphur in Pyrite and Marcasite by a 5 *per cent Solution of* $KMnO_4$ *at* 100° *C.*

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five hour
Pyrite with 5 p c. $KMnO_4$ at 100° C.	7·95	7·52	9·85	11·86	14·98
Marcasite with 5 per cent $KMnO_4$ at 100° C.. ..	8·38	8·38	13·27	14·85	16·36

(To be continued).

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* Read before the American Philosophical Society, May 18, 1894. —From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

A RE-DETERMINATION OF THE ATOMIC WEIGHT OF YTTRIUM.*

By HARRY C. JONES.

THE separation of those elements which occur together in such minerals as gadolinite, samarskite, &c., has always been a matter of considerable difficulty, due largely to the close agreement in the properties of the elements in question. As a consequence of this, what were at one time supposed to be elementary substances have since been shown to be mixtures of two and in some cases of a group of elements, whose compounds were so closely allied in properties as to escape the chemical methods of separation which had been employed.

Spectrum analysis, which has been so fruitful in other fields, has been of value here in showing that the substances which were supposed to be individuals were really mixtures. The atomic weights of these rarer elements have been determined from time to time by analysing their compounds which were thought to be pure, with the result that widely different values have been found for the same element, by different experimenters using different preparations of what was regarded as the same substance. This is well shown in the case of yttrium, whose atomic weight as determined varies from about 105 to 89·1. This is not surprising, since it seems now to be pretty well established that only in one or two cases has even a fairly pure yttrium compound been obtained and used.

This but serves to show that, while the atomic weight of most of the more common elements can be regarded as known to within comparatively narrow limits, the atomic weight of some of the rarer elements may not yet have been correctly determined to within several units.

We need better methods for separating these mixtures, that we may obtain purer compounds from which the atomic weights of the elements can be determined, and any step which will aid us in this direction cannot be without some interest and value.

A method more satisfactory than any hitherto employed for separating yttrium from many of the constituents which occur with it seems to have been found by Prof. Rowland in connection with his study of the spectra of the rarer elements. Although an account of this method has already been published (*Johns Hopkins Univ. Circular*, cxii., 73; reprinted in CHEM. NEWS, lxx., 68), yet it is desirable to cite here that part of it which has to do directly with the separation of yttrium by the use of potassium ferrocyanide.

"This is the most useful process, and easily separates the element (yttrium) pure and free from all others. To obtain pure yttrium from the mineral gadolinite, fergusonite, or samarskite: First obtain the crude mixed earths in the usual manner; then separate the cerium group as usual until the absorption bands of neodymium

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* *American Chemical Journal*, vol. xvii., No. 3.

no longer appear. For the complete separation without loss this must be done several times, as much of the yttrium group is carried down with the first precipitate. * * * * *

"The separation of the yttrium from the other elements is effected by precipitating the latter from a weak acid solution by potassium ferrocyanide. For this purpose the filtrate, after separating the cerium group, can be used at once by slightly acidulating with nitric acid, diluting, and adding a weak solution of potassium ferrocyanide. No precipitate should appear at once, but on standing for an hour or so some will come down. Add more potassium ferrocyanide, and repeat until the filtrate no longer shows the bands of so-called erbium. After this it is best to precipitate with oxalic acid or potassium oxalate, and ignite the precipitate so as to get the earth. Dissolve this in nitric acid, and add only water enough to make a very concentrated syrupy solution. Place in a beaker at least 3 inches in diameter, and examine with a spectroscope of low power for absorption bands. Probably the bands of neodymium and "erbium" will appear. Separate the first by sodium sulphate as usual, and the last by potassium ferrocyanide from an acid solution as above. The filtrate will then contain the pure yttrium, whose calcined oxalate will be pure white without trace of yellow. After separation of iron, calcium, and possibly manganese, the earth will be a pure element, as far as I can tell, spectroscopically. However, like Zr, Fe, and many other substances, the addition of Na or K to the electric arc, while obtaining the spectrum, will change the intensity of certain lines of the spectrum, while others are unchanged. If this is considered as evidence of the existence of two elements, then the same evidence will apply to Fe and Zr. The reason for believing that the substance thus found is an element is based on the fact that its spectrum remains unaltered in all minerals, and after all chemical operations, that I have been able to devise. Furthermore, I believe that the new process is not only more easy than any other, but also that it has given a single element for the first time. * * * The yield will, of course, depend on the amount of purity required. From the earths of gadolinite about one-tenth of quite pure yttrium can be obtained and about one-twentieth of very pure.

"I have determined spectroscopically that when, by the above process, the absorption band of "erbium" at last disappears from 3 inches of strong solution, all the other elements have also disappeared.

"By taking the first precipitate several times by potassium ferrocyanide from an acid solution, a mixture of many elements is obtained which contains much of that element to which the so-called "erbium" band is due. By dissolving a weighed quantity of this mixture in nitric acid and water, and examining the band spectrum, I have determined the limit when the band can no longer be seen. Thus I have proved that when the band vanishes from 3 inches of concentrated syrupy solution of yttrium, there cannot exist in it more than ½ per cent of the mixed element as compared with the yttrium, and there is probably less.

"I have not found potassium ferrocyanide useful in the further separation of the elements, but only in separating out α (yttrium) from the others.

"When the neodymium band has disappeared by use of sodium sulphate, all the other elements of the cerium group have disappeared. The element thorium is sometimes present in the crude earths, but disappears after a while from the purified earths. The conditions for its disappearance I have not determined."

A specimen of yttrium oxide, purified by the above-described process, was furnished me by Prof. Rowland for the purpose of determining the atomic weight of yttrium. While the yttria was free from all other rare elements with certainty to within ½ per cent, and probably to within much less, yet the spectrum showed that it might contain traces of calcium, magnesium, iron, and manganese. To remove the traces of these impurities, if present in the yttria, the latter was dissolved in strong nitric acid, and the excess of acid evaporated off on the water-bath. The slightly acid solution was then diluted with a large volume of water, and the yttrium precipitated from the hot solution by ammonia from which all carbonate had been removed, as yttrium hydroxide. The hydroxide precipitated in this manner is somewhat gelatinous, but is more easily filtered and washed than when precipitated from a cold solution. To wash the yttrium hydroxide thoroughly was a somewhat tedious process. The precipitate was allowed to settle, and the supernatant liquid decanted as completely as possible. The precipitate was then treated again with hot water, well shaken, and allowed to settle. The water was again decanted, and the process repeated many times until the precipitate seemed to have been well washed. A small quantity of the hydroxide was then brought on the filter and washed many times with boiling water; this was removed, another small quantity filtered off and washed, and this continued until all of the yttrium hydroxide had been finally washed in this manner. By this process any calcium or magnesium would have been separated from the yttrium.

The yttrium hydroxide was then dissolved in nitric acid and the yttrium precipitated from the acid solution by oxalic acid, which had been repeatedly crystallised from cold water, as yttrium oxalate. The crystalline oxalate was brought on the filter also in small quantities, washed well with hot water, and dried in an air-bath. The dry oxalate was ignited in a platinum crucible over the blast-lamp until the pure oxide remained. In this way any iron or manganese would have been separated from the yttrium.

The yttria thus obtained from the oxalate was pure white when heated over the blast-lamp for a short time. After prolonged heating at a very high temperature it seemed to me to acquire a faint yellow tint. Another observer declared, however, that he was unable to detect a trace of yellow.

The oxide which had been heated for a short time as well as that which had been heated more vigorously, was tested for calcium, magnesium, iron, and manganese by chemical tests, but these failed to show the presence of either of the above-named elements in the yttria.

About 6 grms. of yttria were thus obtained free from all the more common elements and containing as a maximum impurity ½ per cent of the rarer oxides. This is the yttria which was used in the following determinations.

The platinum crucible in which the yttrium oxalate was decomposed to the oxide and which was used throughout the work, was carefully cleaned, and finally, in order to remove any iron which might distil out into the yttria, was heated for a long time in the vapours of ammonium chloride.

All weighings of the platinum crucible, either when empty or when containing the yttrium compound, were made with the crucible placed within a ground-glass stoppered weighing-tube for protection from the atmospheric moisture. This was necessitated by the hygroscopic character of the anhydrous yttrium sulphate. The crucible with its contents was placed in the weighing-tube, while still warm and the tube closed. Further cooling took place in a desiccator over calcium chloride. The stopper was removed from the tube for an instant just before weighing, to insure equalisation of the air pressure. All the weighings were reduced to a vacuum standard. A long-armed Becker balance was used and the accuracy of the weights insured by previous comparisons.

I. *Conversion of the Oxide into the Sulphate.*

The platinum crucible was heated over the blast-lamp to constant weight. The desired amount of yttria, which had been already well ignited, was placed in the crucible and heated again for a short time over the blast-lamp. It was then weighed, re-heated, and re-weighed. In no case was any loss in weight detected, due to the second heating.

The oxide in the platinum crucible was then treated with sulphuric acid of the concentration 1 acid to about 3 of water, and placed in an ordinary air-bath and warmed gently until most of the excess of sulphuric acid had evaporated. The sulphate usually began to crystallise from the solution before all the oxide was dissolved. For this reason large amounts of oxide could not be employed in any single determination, since, with large quantities, one could not be certain that all the oxide had been transformed into sulphate. In one or two of the determinations made there was some doubt on this point, but, that the oxide was completely converted into sulphate in all of the determinations, the results of which are given below, is shown by the fact that the sulphate was found in each case to be entirely soluble in water. The crucible containing the yttrium sulphate, a little free sulphuric acid, and, probably, some acid sulphate, was then placed in an air-bath of such a form that it could be more highly heated than before. This bath consisted of a cylinder of copper about 12 c.m. high and 10 c.m. in diameter, into the opposite sides of which two large holes had been cut and covered with plates of mica. This enabled one to see through the bath at all times. A thick plate of copper was riveted on to the bottom and allowed to project on all sides about an inch beyond the cylinder, to prevent reducing gases from the flame from entering the bath and coming in contact with the yttrium compound. The top of the bath was covered with a plate of iron, and this in turn with a sheet of asbestos. The platinum crucible was supported on a porcelain triangle about an inch from the bottom of the bath. The bath was heated by two triple burners to a little above the boiling-point of sulphuric acid. This removed all free sulphuric acid and decomposed any acid sulphate which might have been present, as was shown by testing a solution of the sulphate in water with methyl-orange, with which acid sulphates give an acid reaction. The sulphate was heated in this bath to constant weight. That there was no decomposition of the sulphate into basic sulphate was indicated by the two facts, that constant weight was quickly established and that the resulting sulphate was entirely soluble in water.

When the anhydrous sulphate was brought in contact with water the greater part of the salt dissolved at once, while a small portion took up water and passed over into the crystalline salt with water of crystallisation. The crystalline sulphate is less soluble than the anhydrous, but on heating the solution every trace of it is dissolved.

A few determinations by this method were lost by accident. In one or two cases, where larger amounts of oxide were employed and not a very great excess of sulphuric acid, the sulphate, when dissolved in water, was found to contain traces of oxide. Below are the results of the ten determinations which were successfully carried to completion:—

	Y_2O_3.	$Y_2(SO_4)_3$.	$3(SO_3)$.	$\left\{ \begin{array}{l} O=16 \\ S=32·06 \end{array} \right\}$ At. wt. yttrium.
I.	0·2415	0·4984	0·2569	88·89
II.	0·4112	0·8485	0·4373	88·92
III.	0·2238	0·4617	0·2379	88·97
IV.	0·3334	0·6879	0·3545	88·94
V.	0·3408	0·7033	0·3625	88·90
VI.	0·3418	0·7049	0·3631	89·05
VII.	0·2810	0·5798	0·2988	88·94
VIII.	0·3781	0·7803	0·4022	88·89
IX.	0·4379	0·9032	0·4653	89·02
X.	0·4798	0·9901	0·5103	88·91
Total	3·4693	7·1581	3·6888	
Average				88·94

The mean value of the ten determinations is 88·94, with a maximum value of 89·05 and a minimum value of 88·89. The atomic weight of yttrium, calculated from the total oxide used, 3·4693 grms., and the total sulphate found, 7·1581 grms., is 88·94. All of the above and following calculations are based on oxygen = 16, and sulphur = 32·06; $SO_3 = 80·06$.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 22nd, 1895.

Mr. R. T. Glazebrook, M.A., F.R.S., in the Chair.

This meeting was held at the Royal College of Science, South Kensington.

"*On the Objective Reality of Combination Tones.*" By Prof. A. W. Rücker and Mr. E. Edser.

The question as to the objective or subjective nature of combination tones has excited much keen controversy, and the authors have devised some experiments to elucidate this point. These experiments, some of which were exhibited before the Society, show that, under certain conditions, difference and summation tones are produced which are capable of disturbing resonating bodies. As resonator they have, in the first instance, employed a tuning-fork. A piece of thin wood, about 5 inches square, is attached to one of the prongs of a tuning-fork, while a silvered glass mirror is attached to the other, and the pitch is very accurately adjusted to 64 complete vibrations per second. In order to detect any movement due to resonance set up in this fork, the mirror carried by the prong forms part of a system of mirrors for producing Michelson's interference bands. By this means a movement of the prongs of the fork of 1/80,000th of an inch (half a wave-length of light) is shown by the disappearance of the interference bands. As a source of sound a siren was employed, this being one of the instruments which Helmholtz recommends as giving the best results. The pitch of the notes given by the siren was adjusted by noting the disappearance of the beats produced by one of the notes with a bowed fork, or by a stroboscopic method. A large wooden cone, placed between the siren and the resonating fork, served to concentrate the sound on the wooden disc attached to this latter. The sensitiveness of the arrangement is such that when a large Kœnig standard fork, giving 64 vibrations per second, is struck so lightly that an observer with his ear close to the fork cannot detect the fundamental note, the bands instantly disappear. The apparatus, however, is unaffected by any other note, except one of 64 vibrations per second. A number of experiments have been made using various rows of holes on the siren, and in every case when the summation or difference tone corresponded to 64 vibrations per second the interference bands vanished, showing that under the condition of the experiment these tones have an objective existence. An experiment has also been made to determine whether Kœnig's lower beat tone, where the interval is greater than an octave, is objective. In this case, however, the authors entirely failed to get any evidence of such an objective existence. A number of experiments have been made with a view to elucidating the cause of the production of the summation tone, which tend to show that it is not the difference tone of the partials of the fundamental notes. In addition to using a tuning-fork to detect the combination tones, the authors have made use of an instrument which was originally devised by Lord Rayleigh. A light mirror is suspended by means of a fine quartz fibre, and hangs in the neck of a resonator, tuned to the given note, and when at rest is inclined at 45° to the axis of the resonator. Under these circumstances, when the resonator responds, the mirror tends to turn and set itself at right angles to the direction of motion of air in the resonator. The results obtained with this instrument are in complete accord with those obtained by the first method. Up to the present the authors have failed to obtain any evidence of the objective reality of the combination tones produced by organ-pipes and tuning-forks.

The discussion on this paper was postponed till after the reading of the next paper.

"*Some Acoustical Experiments.*" By Dr. C. V. BURTON. (1.) On the Subjective Lowering of Pitch of a Note.

The author has noticed that if a tuning-fork, mounted on a resonator, is strongly bowed, then, if the ear is placed near the opening of the resonator, the pitch of the note heard appears lower than when the fork is bowed very gently or is held at some distance. This subjective lowering of pitch is most marked with forks of low pitch, and, in the case of a fork giving a note of 128 complete vibrations per second, amounts to about a minor third. The author suggests an explanation depending on the supposition that the basilar membrane of the ear behaves as if it consisted of a number of stretched strings of various lengths, each resounding to a given note, and that the appreciation of the pitch of a note depends on the localisation of the part of the basilar membrane which resounds most strongly. Further, he shows that in the case of a stretched string for finite displacements, the string which most strongly resounds to any given note will have a "natural" period longer than the period of the disturbance; the greater the disturbance the longer will be the natural period of the strings most strongly affected. Hence when the intensity of a note increases, the tract of the basilar membrane most strongly affected is displaced in the direction which corresponds to the perception of lower notes.

(2.) Objective Demonstration of Combination Tones.

When two organ-pipes are sounded and alternately separated and brought close together, an observer, at some distance, hears the difference tone much more clearly when the pipes are close together than he does when they are separate. As the position of the pipes with reference to his ear does not appreciably change, the change in the intensity of the combination tone indicates that it has a real objective existence. The author mentioned that he had sounded his two pipes, which give a difference tone of 64 vibrations per second, before the collector of Prof. Rücker and Mr. Edser's apparatus, but without obtaining any motion of the interference bands, and that he was therefore less confident of the correctness of his deductions than he had been before.

Mr. EDSER mentioned that Dr. Burton had suggested an explanation of the production of objective tones in the use of the siren which depends on the production of the tones in the wind-chest of the instrument itself, when two rows of holes are simultaneously opened. They had made an experiment which seemed to show that the above explanation was incorrect, for on connecting together the wind-chests of two sirens, fixed on the same spindle, by means of a short length of wide metal tubing, no effect was observed on the bands when the two notes were produced on different instruments having what was practically a common wind-chest.

Prof. EVERETT (communicated) said he considered the experiments described in the paper proved conclusively the objective existence of the summation tones as distinguished from the supposed beat tones. He had lately been investigating the pitch of the loudest combination tone obtained when two notes having frequencies as 3 to 5 are sounded. Is the frequency of this tone 2, *i.e.*, the first difference tone, or is it 1, which correspondends to the first term of the Fourier series for the periodic disturbance? In the chords 2 to 3, 3 to 4, 4 to 5, &c., the difference of the two integers being unity, the first difference-tone is identical with the first Fourier tone. Where the difference of the two integers which express the chord is not unity, then the writer considers that experiments he has made with strings and pipes show that the first Fourier term is usually the only combination tone that is audible.

Prof. S. P. THOMPSON considered that care should be taken to define what we mean by the subjective or objective existence of a note, and recommended the use of the term "ear-made tone." There are two very delicate methods which have already been employed for detecting the existence of a given note in the air:—1. The formation of ripples on a soap film stretched over the opening of a resonator tuned to the required pitch (Sedley Taylor). 2. The sounds produced in a telephone connected to a microphone placed on a thin elastic membrane stretched over the neck of the resonator (Lummer). It was very important to limit our acceptance of the demonstration of the objectivity of combination tones given by the authors of the paper to the case actually proved, *i.e.*, to tones produced by the polyphonic siren; it did not necessarily follow that if pure tones produced by tuning-forks were used the same results would be obtained. A number of experiments had been made by Zantedeschi in 1857, in which two notes were sounded, and skilled musicians were asked to record their impression of the third tone present. In 75 per cent of the cases the note recorded was the difference tone. In the remaining 25 per cent it corresponded to Kœnig's beat tone. Kœnig himself had never heard the summation tone in the case of lightly bowed forks. Voigt, in a theoretical paper, has shown that if there are two disturbances, whose mean kinetic energy differ, the Helmholtz tones will be produced; but that if the mean kinetic energy of the two disturbances are equal, the Helmholtz effects soon die out, and you get beat tones or beats. He (Prof. Thompson) considered that Dr. Burton had allowed his perception of tone to be governed by the quality of the note, and that the apparent lowering of pitch was due to the variation in the intensity of the overtones present.

In reply to Prof. Thompson, Dr. BURTON said he did not merely perceive a lowering of pitch, but he was able to estimate the change in pitch and say at what instant, as the vibrations of the fork died out, the lowering amounted to a tone or half a tone, &c.

Mr. BOYS said he found that by careful attention he could apparently persuade himself that the note in Dr. Burton's experiment was lowered or raised in pitch, or that it remained unaltered. A similar effect in the case of the eye could be obtained with a stereoscopic picture.

The CHAIRMAN considered that while Helmholtz's explanation of the production of combination tones might be real, it did not follow that this explanation gave the sole cause of their formation. In particular Helmholtz does not explain why the tones should only be produced by some sources of sound.

Prof. RÜCKER, in his reply, said he did not deny the existence of Kœnig's beat tones; in fact, he had heard them. They did not lay much stress on the negative result of the experiment they had made to test the objective existence of these beat tones.

UNIVERSITY COLLEGE, LONDON, CHEMICAL AND PHYSICAL SOCIETY.

March 13th, 1895.

"*On the Metallic Alkyl Compounds.*" By N. T. M. WELSMORE, M.Sc.

After a cursory general review of these substances, the author went on to describe some unsuccessful attempts of his own to prepare magnesium ethide. The only previous references to this substance were:—Hallwachs and Schafarik, *Annalen*, cix., p. 206 (1859); Cahours, *Ann.*

de Chim. et de Phys., lviii., 3rd series, p. 17 (1860); Wanklyn, *Journ. Chem. Soc.*, xix., p. 129 (1866); and Löhr, *Annalen*, cclxi., p. 79 (1891). The author tried heating ethyl iodide with magnesium filings, at ordinary pressure, in carbon dioxide, and also in hydrogen and in sealed tubes; with magnesium-copper couples, prepared in both the dry and the wet way; and with magnesium-sodium alloy and ethyl acetate. In every case, after the ethyl iodide was used up, a white residue remained, from which, however, no liquid but a trace of higher paraffins could be distilled off. The residue turned brown in air, and deliquesced rapidly, and reacted with water with considerable energy, but, contrary to Löhr's account, gave off no gas whatever. An analysis showed it to be nearly pure MgI_2, almost free from metal if excess of ethyl iodide were used; but containing a little organic matter, possibly paraffins, Mg 8·61, I 90·65, C 0·43, H 0·21 (calculated for MgI_2—Mg 8·63, I 91·37). Magnesium iodide thus prepared was freely soluble in boiling anhydrous ether, from which it crystallisedi with apparently two molecules of ether in large prisms. These were, however, so unstable in moist air that satisfactory combustions could not be made. It was probably this substance which Löhr took to be magnesium ethide. The author could only account for the results obtained by this chemist and other previous observers on the assumption that their magnesium contained zinc or some similar impurity. He had also tried heating magnesium with zinc ethide and with mercury ethide in sealed tubes; but the metal did not appear to be attacked. He concluded with the opinion that the alkyl compounds of beryllium and the compound $N(CH_3)_4I_2$, both claimed to have been prepared by Cahours, could likewise not be accepted without further confirmation. Therefore the rule that only elements situated on the rising portions of Lothar Meyer's curve of atomic volumes are capable of forming ethides is, up to the present, without any sufficiently authenticated exception.

NOTICES OF BOOKS.

Ceylon Manual of Chemical Analyses. A Handbook of Analyses connected with the Industries and Public Health of Ceylon. For Planters, Commercial Men, Agricultural Students, and Members of Local Boards. By M. Cochran, M.A., F.C.S., Professor of Chemistry in the Ceylon Medical College, City Analyst to the Municipality of Colombo, Member of the Ceylon Branch of the Royal Asiatic Society. Colombo: A. M. and J. Ferguson. London: Kegan Paul, Trübner, and Co.; Geo. Street and Co.; J. Haddon and Co. 1895.

This work ought to be highly prized not merely by the classes to whom it more directly appeals, but by every true Briton. Tropical and subtropical agriculture is a pursuit in which a large portion of our national capital is invested, and engaging directly or indirectly a still larger proportion of our industry. It may claim our attention the more urgently as it is now attacked on various sides. The parasitic fungi and animalcules of tropical regions, the synthetic chemistry of Germany, the development of rival products, and the frauds of our own merchants, are all tending to reduce the most valuable lands of India, the West Indies, &c., to useless deserts. Hence the instinct of self-preservation should urge us to bring all the resources of chemical and biological science to bear on the questions involved.

To this good task Mr. Cochran here supplies a valuable contribution. He does not attempt to lay down new or special methods of chemical analysis, but gives us results. He gives us, firstly, a view of the composition of the soils and rocks, showing us the conditions under which such determinations are to be trusted. From the data here supplied it would seem that the soils of Ceylon are very rich in quartz and insoluble silicates. He explains the demands made upon the soil respectively by coffee, tea, cinchona, and cacao, and what manures are needed to keep up a supply of suitable plant-food. Unfortunately, as far at least as coffee is concerned, its failure in Ceylon cannot be remedied by any fertilisers, since it is due to a parasitic fungus. This pest is spreading to Fiji, and we fear to Java. Whether a richer manure would enable the coffee trees to resist the enemy remains to be proved, and perhaps chemical research may lead us to some fungoids able to destroy the scourge.

We next pass to cereals, especially rice. The proportion of phosphoric acid in rice is relatively high. According to the analysis of Kellner, Japanese rice is richer in fatty matter than that of America or of India.

A table is here given showing the average composition of cereal grains as produced in different countries, no Ceylon samples having been apparently analysed. Nor do we find any analyses of Australian or African grains.

As regards the cultivation of rice, the author recommends that it should receive nitrogen both in the form of nitrates and of ammoniacal salts. We regret to find that there is no analysis given of the drainage-waters from rice-fields. This water is said to be especially dangerous, and it would be important to know if this opinion is well-founded, and, if so, whether the mischief is due to chemical ingredients or to the presence of morbific organisms.

The products of the coco nut palm are considered at some length. The yearly value of a coco-nut plantation on good soil is said to be £8 15s. per acre. Attention is called to coco-nut butter, an article recently placed upon the market, and in many respects superior to the margarines.

The tea-crop makes a heavy demand upon the potash, and the phosphoric acid in the soil. There is no special mention of the composition of the soil of the "Mazawattee" estate, which is now, acccording to advertisers, producing such a large proportion of the tea consumed in Britain.

The tannin question is not overlooked. Thr author quotes Mr. Hodge for the statement that the finest teas are those which contain most tannin. A short time ago an attempt was made to depreciate Indian and Ceylonese teas in comparison with those of China, on account of the greater proportion of tannin which the former were asserted to contain. The differences which the patriotic (?) authors so eagerly pointed out seemed due not to any inherent difference in the quality of the tea, but to a different manner of preparation.

Cinchona barks are cultivated in Ceylon on a commercial scale, the principal species being *C. succirubra*, *C. officinalis*, and *C. calisaya*. The proportion of quinine in the *succirubra* natural bark is 1·20 per cent, and in the renewed bark 2·73, in addition to cinchonidine, quinidine, and cinchonine.

The cacao grown in Ceylon is chiefly the Caraccas variety, and it is much esteemed for the manufacture of chocolate. Much of it is exported first to America, and thence to Mexico. According to the analysis of Dr. Tatlock, F.R.S.E., it is exceptionally rich in albumenoids and in the characteristic alkaloid theobromine. It is an exhausting crop as regards phosphoric acid.

Into the useful information on tobacco, areca-nuts, arnatto, coca (erythroxylon), cotton, and datura, space does not allow us to enter.

Pepper, opium, indigo, and ipecacuanha do not seem to rank among the agricultural productions of Ceylon.

The latter part of the book is devoted to sanitary analysis. It is remarkable that the only sample of lemonade which came under the author's hands contained a considerable quantity of arsenic! It is noticed that the sender had "merely tasted it"—a fact which raises some difficult questions.

In fine, to all whom it may concern, this book deserves to be warmly recommended.

Calcareous Cements; their Nature and Uses. With some Observations upon Cement Testing. By Gilbert R. Redgrave, Associate of the Institution of Civil Engineers, &c. Small 8vo., pp. 238. London: C. Griffin and Co. (Ltd.). 1895.

This valuable work has its painful feature in as far as it treats of an industry which was until of late years peculiarly British. It has, however, been lost as far as the export trade is concerned, and it may even be threatened at home. The fact is that the Belgian or German cement manufacturer can employ two men at about the same cost as our English makers can employ one, and can consequently offer his product at a lower price.

Mr. Redgrave points out a further disadvantage to which we are subject, but one more easily remedied. In the method of testing cements we are, he states, seriously deficient as compared with our continental opponents. He gives in full the German rules for testing. He condemns, on the authority of many experiments conducted by German manufacturers and engineers, the various additions to the normal Portland cement materials, as proposed by certain inventors, and hopes that they may be brought within the scope of an amended and extended Adulteration Act—a hope in which we most heartily join. In speaking of the use of sewage-sludge as an ingredient in the manufacture of Portland cement, he seems to us to take too favourable a view of the results. He even ventures on the statement that, in the treatment of sewage, "lime is well known to be the cheapest and best precipitating agent." This assertion, except as regards cost, we must beg leave to contradict most emphatically. This, we have pleasure in adding, is the only questionable statement we can find in a work otherwise calculated to be of great and extended utility.

Agricultural Journal, Published by the Department of Agriculture of the Cape Colony. Vol. viii., No. 3, February 7, 1895.

This issue is exceptionally rich in important matters. We notice a paper by Mr. Otto Henning, C.V.S., on the dissemination of echinococcosis of dogs. The dog is the intermediate host of certain tape-worms, the ova of which are often found in multitudes in his excreta, saliva, and other secretions. Hence it is very important that dogs should have no access to wells, conduits, gathering grounds, and reservoirs subserving municipal or domestic water supplies. The original home of the parasite *Tænia echinococcus*, and consequently of the fearful disease which it occasions, seems to have been Iceland, but it has spread to India and Australia, and is now threatening Africa.

The "Sand Dunes of Gascony" is the title of a very instructive paper, describing the overspreading of valuable agricultural lands, forests, and even villages, by drift-sand from the shore. This was formerly a growing danger in the Landes of Gascony. It has been arrested by measures devised by Brémontier and by Grandjean. The principal agent employed is the so called mairom-grass or sea-matweed, *Ammophila arenaria*, followed up by the maritime pine (*Pinus maritima* of Lamarck).

There is a notice of manuring fields by the process of "Sideration," without any notice of the experiments of M. Ville. The writer, moreover, would prefer to feed cattle with the green crops instead of ploughing them in.

There is a short notice of the alleged impunity of man and other animals against snake-bites if they have once been bitten by a death-snake and have recovered. We suspect recoveries from the effects of the venom of the cobra are very doubtful, unless the part has been immediately amputated.

Alumni Report, Published by the Alumni Association of the Philadelphia School of Chemistry. Vol. xxxi., February, 1895.

A speaker at a Pharmaceutical Meeting pointed out the annoyance occasioned by the practice of colouring beet-sugar with ultramarine. If it comes in contact with an acid, hydrogen sulphide is of course liberated.

Much attention is drawn to the necessity of a cheaper and more convenient supply of alcohol for scientific and technical uses. In this country, on the contrary, we submit without remonstrance to the addition of naphtha to methylated spirits, thus rendering it unfit for all scientific and most technical purposes.

CORRESPONDENCE.

NEW HYDROGEN SULPHIDE GENERATOR.

Monsieur l'Editeur des Chemical News.

Dans votre No. 1843, du 22 Mars, Mr. J. J. D. Hinds décrit et figure ce qu'il croit "A New Hydrogen Sulphide Generator."

Il me sera permis sans doute de faire remarquer que cet appareil, dont je ne discuterai ni les avantages, ni les inconvénients pour l'usage auquel son auteur le destine, n'est qu'une copie exacte de celui que j'ai proposé il y a 15 ans pour la préparation du gaz acide chlorhydrique, décrit et figuré dans la *Zeitschr. f. anal. Chem.*, t. xix., p. 467, et planche 5, figure 7.

Espirant que vous voudrez bien publier les lignes qui précédent dans votre important journal, je vous presente, Monsieur l'Editeur, l'expression de mes sentiments les plus distingués.

L. L. de Koninck.

Liége, le 23 Mars, 1895.

BORON CARBON BATTERY.

To the Editor of the Chemical News.

Sir,—In reply to Mr. Reed's letter of March 15 I beg to inform the writer that there is a vast difference between a platinum element and a platinised one. I admit I use a platinised element, which costs one-fiftieth the price of a platinum one. The writer also states that a primary battery capable of giving 3 volts is by no means remarkable: perhaps he would oblige with a description of a few such cells. As regards a further description of the cell I shall only be too willing to publish this, together with further improvements, when time permits.—I am, &c.,

H. N. Warren.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

Study of the Iron Chromates.—Charles Lepierre.—The author, when studying the action of the different rays of light upon the chromogenic power of microbia, employed a mixture of ferric chloride and of potassium dichromate as a liquid for absorbing the yellow and orange rays. In the course of some days the sides of the vessel were lined with red crystals, the formation and the composition of which had not been observed and determined. He examined separately the results obtained with ferrous and ferric salts. Concerning the analysis of the products, he states that the elimination of the chrome existing in the solution in the form of alkaline chromate is absolutely useless, since, in the analysis of celestine, a mixture of the salts of strontium and calcium, on the addition of ammonium or potassium chromate, does not give a precipitate of chromate, and the subsequent addition of ammonia and ammonium carbonates precipitates carbonates, and not chromates.—*Bull. Soc. Chim.*, xi.-xii., No. 23.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 10, March 11, 1895.

Argon.—M. Berthelot.—Already inserted.

Losses of Nitrogen caused by Waters of Infiltration.—M. Schlœsing.—The quantities of nitrogen thus carried off are much smaller than we have been led to suppose from the determinations of nitric acid in the drainage waters hitherto published. The losses of nitric acid are distributed very unequally in our fields. Nitrification depends on the organic matter, and is active or slow according to its proportion. Thus the loss of nitrogen is like a graduated tax which falls slightly upon poor soils, and only increases with the richness of the fields.

Analysis of Oyster Shells.—A. Chatin and A. Murtz.—Nitrogen forming part of the organic frame-work of the shells, 0·01 grm.; silica, chiefly in the nacreous layer, 0·07; sulphur, as sulphuric acid, 0·15, besides sulphur in the state of sulphide or in animal compounds, 0·02 grm.; magnesia, 0·4 grm.; manganese, 0·012 grm.; iron, 0·025 grm.; animal matter forming a frame-work in which the mineral substances are deposited; fluorine, about 0·020 grm.; bromine, nearly 0·005 grm.; iodine, 0·003; chlorine, totally absent; carbonic acid, $\frac{45}{100}$ to $\frac{48}{100}$. Phosphoric acid, in common oysters, from 0·03 to 0·04 grm., but in Portuguese oysters (*Gryphea angulata*), 0·075. The proportions of iodine and phosphorus may explain the use of oyster shells in the medical practice of the Middle Ages.

Analysis of Silicon.—M. Vigouroux.—If we allow potassium to act upon a silico-fluoride, there are produced a series of reactions analogous to those indicated by Moissan in the preparation of boron by means of the alkaline metals. A great part of the nascent silicon combines with the potassium in excess, and the iron in which we operate. If we afterwards treat the product of the reaction with water, whilst a further quantity of silicon disappears and is converted into silica in favour of the alkaline metal which has not reacted, the insoluble foreign matters increase the proportion of impurities (silicon, hydrogen, potassium, iron, &c., silicides). In the preparations of amorphous silicon, it seems preferable to use infusible and inert matters, such as silica and magnesia.

Action of Formic Aldehyd upon Ammoniacal Salts.—A. Brochet and R. Cambier.—The authors study the action of ammonia hydrochlorate, both in the cold and in heat. They infer that there exist between ammonia and hexamethyleneamine one or more bases serving as intermediate terms. They are not isolable, but we have been able to demonstrate their existence by the acidimetric study of the solutions, and by fixing these bases in insoluble compounds, such as chloroplatinates or nitroso-derivatives. The other ammoniacal salts give with formaldehyd similar results.

On the Acid Chlorides and Chloro-aldehyds.—Paul Rivals.—A thermochemical paper not susceptible of abstraction.

Splitting Up the Butane-2-oleïc Acid (α-Oxybutyric Acid).—Ph. A. Guye and Ch. Jordan.—The authors have split up this acid into its two components, dextro-rotatory and lævo-rotatory. The separation of these two active isomers is effected very distinctly by the crystallisation of the brucine salt. The crystallisations were effected at temperatures not exceeding 10°, the lowest appearing favourable to the separation.

Daturic Acid.—E. Gérard.—A controversial paper upholding the existence of daturic acid as a chemical individual, $C_{17}H_{34}O_2$, intermediate between the palmitic and the stearic acid, in opposition to J. Dupont, who has recently ("Supplément au Dictionaire de Chimie," by Wurtz) pronounced it a mere mixture of fatty acids. The view of E. Gérard is supported by Noerdlinger and by Wanklyn and Johnstone.

Glycogen in the Blood in Animals in Health or Diabetic.—M. Kaufmann.—The author shows that glycogen is a constituent of normal blood, whilst the blood of animals rendered diabetic by the extirpation of the pancreas contains glycogen in a much more considerable quantity.

Signification of the Liberation of Carbonic Acid by Muscles Isolated from the Body compared with that of the Absorption of Oxygen.—J. Tissot.—There is a complete disagreement between the indications yielded by the quantities of carbonic acid given off and those of oxygen absorbed. The total quantity of carbonic acid disengaged by a muscle isolated from the body cannot be taken as the measure of the physiological activity of this muscle. The absorption of oxygen alone is closely linked to the manifestation of this activity.

Bulletin de la Société Chimique de Paris. Series 3, Vols. xi.-xii., No. 24, 1894.

New Element obtained from Red French Bauxite.—Dr. R. S. Bayer.—Already inserted.

Singular Case of Metallic Precipitation.—J. B. Senderens.—The author (*Soc. Chimique*, May 20, 1894) has observed that metallic lead was deposited upon bars of lead suspended in a neutral solution of lead nitrate at the ordinary temperature. He thinks that the bars of lead may form a galvanic couple, the interior crystals forming one of the elements, and the superficial layers the other.

On a Lead Orthonitrate.—J. B. Senderens.—The orthonitrate has the composition $(NO_4.HPb)_4+H_2O$.

Researches on the Mercuric Sulphates.—Raoult Varet.—A thermochemical paper not adapted for useful abstraction.

Superposition of the Optical Effects of Various Asymmetric Carbons in one and the same Active Molecule.—A. Guye and M. Gautier.—Already inserted.

Active Hydrocarbides with Amylic Radicles.—Miss I. Welt.—The rotatory-power of diamyl is about double that of the foregoing terms. This result is conformable to the ideas developed by Guye and Gautier, according to which the rotatory-power of a substance containing two identical asymmetrical carbons, such as diamyl, must be equal to double the rotatory-power of a diamyl containing an active and an inactive amyl radicle.

Sulphonic Colouring Matters derived from Triphenylmethane.—Maurice Prudhomme.—The sulphonic derivatives of the diamido- and triamidotriphenylcarbinols are colouring-matters known as acid malachite green, acid magenta, alkaline blue, &c. The solutions of these colours, which have a remarkable intensity, are totally decolourised by caustic alkalis. The author concludes that:—1. The alkaline salts of the sulphonic diamido- and triamido-triphenyl carbinols represent, in a state of purity, the colouring-matters known under the general name of acid magentas. 2. The groups $(C_6H_3 . SO_3Na . NR_2)$ in them are electropositive; the OH, connected directly to the methanic carbon, is of an acid nature, capable of exchanging its atom of hydrogen for an atom of sodium in presence of caustic soda or sodium carbonate.

MEETINGS FOR THE WEEK.

Monday, April 1st.—Society of Arts, 8. (Cantor Lectures). "Commercial Fibres," by Dr. D. Morris.
—— Society of Chemical Industry, 8. "The German Patent Laws and their relation to Home and Foreign Inventions," by Dr. Carl Pieper.
Tuesday, 2nd.—Royal Institution, 3. "The Internal Framework of Plants and Animals," by Prof. Charles Stewart, M.R.C.S.
—— Institute of Civil Engineers, 8.
—— Pathological, 8.30.
—— Society of Arts, 8. "My Recent Voyage in Siberia," by Capt. Wiggins.
Wednesday, 3rd.—Society of Arts, 8. "Sand Blast Processes," by John J. Holtzapffel.
—— Geological, 8.
Thursday, 4th.—Royal Institution, 3. "Animism, as shown in the Religions of the Lower Races," by E. B. Tylor, F.R.S.
—— Institute of Electrical Engineers, 8.
—— Mathematical, 8.
Friday, 5th.—Royal Institution, 9. "Argon," by Lord Rayleigh.
—— Quekett Club, 8.
—— Geologists' Association, 8.
Saturday, 6th.—Royal Institution, 3. "Waves and Vibrations," by Lord Rayleigh, F.R.S.

THE CHEMICAL NEWS.

VOL. LXXI., No. 1845.

A REFORM IN CHEMICAL, PHYSICAL, AND TECHNICAL CALCULATIONS.

By C. J. HANSSEN, C.E.

THE study of chemical and physical science, the understanding of the principles involved in chemical and physical phenomena and problems, and the rational application of the results of scientific investigation to practical purposes, would be made easy, if the observations related to these subjects, especially the weight of aëriform substances, were expressed and recorded in a more plain, uniform, and international manner than hitherto. In text-books and publications we find that hardly two authors agree in their statements of specific gravities and specific heats, especially of aëriform substances. Some authors reduce their weights to the 45° latitude and sea-level, others to the latitude and elevation of London, Paris, Berlin, &c. Some prefer the English standard weights and measures and the Fahrenheit thermometer, others the metric weights and measures and the Centigrade thermometer; while some even use both systems in one evening's lecture. In short, a great and serious confusion prevails in these matters, and last, but not least, some of the great masters in the science of heat find wide differences between their calculations and the results of their experiments.

In the following pages the author will endeavour to show that the troubles mentioned can be got over in a very plain way, and to explain a method by which a great many difficult problems may be solved by simple arithmetical calculation, and with greater exactness than by any more elaborate method.

Terms and Units.

The proposed reform and method of calculation requires the use of a system of measure and weight which gives a simple relation between the unit of length (which determines volume), the unit of mass, and the unit of specific gravity. Such a relation is found in the metric system of measure and weight; and this system, therefore, may be used in the proposed method of calculation, and is used here, as no decimal system of measure and weight based on the Anglo-American units as yet is adopted and authorised.*

The *unit of relative gravity* of aëriform substances should be *hydrogen*, because atmospheric air, now commonly adopted as unit, is not a simple substance, but a mixture of at least four different gases, whose proportions are subject to frequent changes, and therefore its gravity is not constant; moreover, its relations to other gaseous substances and to water can only be *approximately* expressed by a long row of decimals, which are tedious to manipulate.

The proper unit of gravity is *hydrogen*, but it is extremely difficult to find the weight of hydrogen accurately by experiment; it is therefore advisable to calculate it from the weight of oxygen and nitrogen, which now have been determined with great accuracy. But even a suitable unit would be useless if its value were not adopted universally. Astronomers of all nations find it advisable and convenient to adopt the meridian which passes through the observatory of Greenwich as the first, and to refer all observations of longitudes to that meridian. In a similar way, physicists and chemists of all nations must adopt a common *circle of latitude*, and all observations and calculations on gravity must be reduced to that latitude. An enormous saving of time and trouble would be the result of this simple measure.

The *weight* of *oxygen* of 0° C. and atmospheric density, as determined by Regnault, is per cubic metre—

		Kilogrms.
At 45° latitude and sea-level	.. ..	1·42909
In Paris	48° 50′ 11·2″ and 60 metres above sea	1·42913
In LONDON	51° 30′ 49″ ,, 50 ,, ,,	1·42991
In Berlin	52° 30′ 16·7″ ,, 40 ,, ,,	1·43003

The weight of a cubic metre gas decreases from north to south, and at a certain latitude, near the 42°, and 0 metres above sea, it will be 1·4285714285 kilogrms.; or exactly 1/700 of 1000 kilogrms., or of 1 cubic metre of distilled water of 4° C. = 10/7 kilogrm. per 1 cubic metre of oxygen

Nitrogen.—At the Royal Society's meeting, January 31, 1895, it was stated that three samples of chemical nitrogen, prepared from different compounds, had been found to weigh 1·2505 grm. per litre in the mean, but that the heaviest sample was about $\frac{1}{1000}$ heavier than the lightest, and that it was very difficult to free the N entirely of argon. It, therefore, is likely that a litre of *absolutely pure nitrogen* weighs 1·250494 grms.

Assuming this, and taking the atomic weight of N = 14, we get the weight of 1 litre

$$\textit{hydrogen} = \frac{1{\cdot}250494}{14} = 0{\cdot}089321 \text{ grm.}$$

This weight certainly is rather less than hitherto accepted, but 1 volume argon in 4000 volumes of hydrogen would make up the difference, and this minute admixture of A would be difficult to detect and remove.

Oxygen.—The weight of 1 litre of oxygen we find then 0·089321 × 16 = 1·429136 grms., and the weight of 1 litre *Argon* = 0·089321 × 20 = 1·78642 grms.
Multiplying the weights per litre so found by the coefficient 0·999605, to reduce them to weight at the latitude of international gravity, we find at 0° C. and atmospheric pressure the absolute and relative weights. (See Table).

The specific gravity of solid and liquid substances is equal to the absolute weight of 1000 c.c. or 1 litre of the substance, the weight of distilled water at 4° C. being = 1.

Unit of Work.—1 kilogrm. or litre distilled water at 4° C. lifted 1 m. high, = 1 metre-kilogrm.

At the circle of international gravity, where 1 cubic metre oxygen (of atmospheric density at freezing temperature of water, 0° = 273° absolute) weighs 10/7 kilogrms. will be:—

Atmospheric mean pressure = 759·72353 m.m. of mercury. This to be called normal atmosphere; barometric scale to be divided into 1000 parts and pressures denoted: 1·095 atm. N, &c.

1 atm. N = 10·330442 m. column of water = 10330·442 kilogrms. per sq. m. = 8113·5119982 kilogrms. per circular m.

Weight of—		Grms. per litre.	Coeff.		Grms. per litre at international latitude.		
Hydrogen	1	0·089321 ×	0·999605	=	0·08928571 =	5/56	grms.
Oxygen	16	1·429136 ×	,,	=	1·428571428 =	80/56 = 10·7	grms.
Nitrogen	14	1·250494 ×	,,	=	1·24999994 =	70/56 = 4/5	,,
Carbon	12	1·071852 ×	,,	=	1·07142852 =	60/56 = 15/14	,,
Argon..	20	1·786420 ×	,,	=	1·78571420 =	100/56 = 25/14	,,
Water (liq.) 4° C.	112·0			=	1000·0000000	= 1000	

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* See "A System of International Measure and Weight," by C. J. Hanssen (CHEMICAL NEWS, vol. lxiii., p. 215).

Boiling-point of Water 99·975° *C.*—Thermometric scale from freezing to boiling-point divided into 100° normal temperature (100° N).

Unit of Heat.—1 kilogrm. = 1 litre water heated 1° N = 1 *calor.*

Dynamic Equivalent of Heat.— 1 calor = 423·813 m.kilogrms.

Proportion between specific heat of gases at *constant pressure* and constant volume=

$$\gamma = 17 : 12 = 1{\cdot}4166666 : 1{\cdot}000000.$$

Expansion of aeriform substances $\frac{1}{273}$ for every 1° N.

Absolute zero of temperature = −273° N.

For *compound gases and vapours* the calculation of absolute weight, atomic weight, and relative weight is thus:—

Water (vapour) of 273° absolute (0° C.) and atmospheric density H_2O.

2 cbm. hydrogen at 5/56 kgs. = 10/56 kgs. combine with
1 ,, oxygen = 80/56 ,, forming

2 ,, vapour of water = 90/56 ,, ; consequently
1 ,, ,, ,, weighs 45/56 ,, and consists

of $1\frac{1}{2}$ cubic metres of simple gases, and 1 kilogrm. of vapour contains 56/45 cubic metres, and consists of 1/9 kilogrms. of hydrogen and 8/9 kilogrms. of oxygen; or of $56/5 \times 1/9 = 56/45$ cubic metres of hydrogen, and $7/10 \times 8/9 = 56/90$, or 28/45 cubic metres of oxygen of 273° absolute and atmospheric density.

The *relative weight* of the vapour (hydrogen being = 1) is found by the proportion—

5/56 kgr. (H) : 45/56 kgr. (vapour) = 1 (H) : 9 (vapour).

Ratio of Chemical Contraction.—In combining to form vapour the 3 cbm. of simple gases have contracted into 2 cbm.; consequently, the ratio of contraction is 3 : 2.

The *atomic weight* of the compound is found by the proportion—

Original volume of simple gases : ultimate volume of compound = relative weight : atomic weight = 3 : 2 = 9 : 6.

Composition of Liquid Water.—By weight, as shown above, hydrogen is 1/9 and oxygen 8/9 of the weight of vapour, and, consequently, also of liquid water. 1 cubic metre of liquid water of 4° C. (273° absolute) weighing 1000 kilogrms. consequently consists of—

Kgs.	Kgs.	Kgs.		Cbm.
$1000/9 =$	$111\frac{1}{9} =$	111·111111	or $11200/9 =$	$1244\frac{4}{9}$ hydrogen.
$8000/9 =$	$888\frac{8}{9} =$	888·888888	or $5600/9 =$	$622\frac{2}{9}$ oxygen.

1000 water = 1 cbm. consists of $1866\frac{2}{3}$ cbm. of simple gases, and the *relative weight* of liquid water, as compared to hydrogen, is found by the proportion—

1000 kilogrms. (water) : 5/56 kilogrms. (hydrogen) = 5600 : 5 = 11200.

The *atomic weight* of liquid water is found by the proportion—

$$\left.\begin{array}{l}\text{Volume of}\\ \text{simple gases}\\ \text{in 1 cbm. of}\\ \text{compound}\end{array}\right\} : \text{1cbm. hydrogen} = \left\{\begin{array}{c}\text{relative}\\ \text{weight of}\\ \text{com-}\\ \text{pounnd}\end{array}\right\} : \left\{\begin{array}{l}\text{atomic}\\ \text{weight}\end{array}\right.$$

$$1866\tfrac{2}{3}\text{ cbm.} : 1\text{ cbm.} = 11200 : 6$$

The *volume of steam* of atmospheric density and 0° C. (273° absolute) would—if steam of atmospheric density could exist as *steam* at that temperature—be found thus—

1 cubic metre water consists of $1866\frac{2}{3}$ cubic metres of simple gases of atmospheric density and 0° C. (273° absolute). In combining, these contract at the ratio 3 : 2, and consequently form $2/3 \times 1866\frac{2}{3} = 1244\frac{4}{9}$ cubic metres vapour, of the initial temperature and pressure of the component gases.

At the boiling temperature of water, 100° C. = 373° absolute, the $1244\frac{4}{9}$ cubic metres of steam would expand to

$$\frac{1244\frac{4}{9} \times 373^\circ\text{ N}}{273^\circ\text{ N abs.}} = 1700{\cdot}2849 \text{ cubic metres}$$

saturated steam of atmospheric pressure of 1 cubic metre water; or exactly—

$$\frac{1755}{2984} \text{ cubic metres}$$

steam of that temperature and pressure, consequently are formed of 1 kilogrm. water and 1 cubic metre of such steam weighs exactly

$$\frac{2984}{1755} \text{ kilogrms.}$$

From the foregoing it follows that steam of any given pressure and temperature always is nine times the weight of an equal volume of hydrogen of equal pressure and temperature.

Atmospheric Air.—The discovery of *argon* calls for a revision of the composition of air. At international latitude, atmospheric density, and 0° N, I calculate—

1 cubic metre air (purged of CO_2) weighs 1·2925977 kilogrms., and contains—

			Grms.	Grms.
208880 c.c.	O	at 1/700 =	$298\frac{2240}{5600}$ =	298·4000
781231 ,,	N	at 1/800 =	$976\frac{3017}{5600}$ =	976·5388
9889 ,,	Argon	at 1/560 =	$17\frac{3690}{5600}$ =	17·6589
1000000 ,,	= 1 cbm. air =		$1292\frac{3347}{5600}$ =	1·2925977 kilogrms.

and 1 kilogrm. air (purged of CO_2) contains—

161597·08768 c.c.	O	at 1/700 grm.	=	230·85300 grm.
604388·42592 ,,	N	,, 1/800 ,,	=	755·48550 ,,
7650·48640 ,,	A	,, 1/560 ,,	=	13·66150 ,,
773636·00000 c.c. air (purged of CO_2)			=	1000·00000 grm. = 1·0000 kgr.

1 grm. = 773·636 c.c. air.

The N and A are mixed in the proportion 79/80 N + 1/80 A (by volume).

3, Valdemarsgade, Copenhagen, V.,
March 4, 1825.

(To be continued).

A WAX FOUND IN THE TREATMENT OF COTTON AND LINEN FIBRE FOR THE MANUFACTURE OF PAPER.

By CLAYTON BEADLE.

It is occasionally observed that the iron walls of a beater in which cotton and linen pulp is disintegrated becomes coated with a film, which protects the iron against the action of the bleach, &c. It appears that this film is not formed under ordinary conditions of treatment, as its occurrence is not generally known to paper-makers. This wax-like film, when of sufficient thickness, can be readily scraped from the sides of the beater. A case of this formation was brought before my notice about two years ago. The formation of this film was so rapid as to cause inconvenience, and to necessitate constant scraping of the sides of the beaters, lest portions should detach themselves and form yellow spots in the pulp.

I examined samples of this substance taken at different times, and found that it consisted of alumina, iron, and lime salts, mixed with a substance soluble in ether. The latter substance has a sweetish smell and generally resembles bees'-wax. It has a saponification equivalent (p.c.) of 19·46 (KOH), and a very definite melting-point of 47·5° C. The wax on saponification gave 91·04 per cent insoluble fat acids. Samples were taken and examined at different times, and were found of constant composition. The raw material that gave rise to the formation of this substance had been previously treated under pressure in a 3½ per cent solution of $NaOH$, and afterwards thoroughly bleached in calcium hypochlorite solution at 32° C. The wax doess not make its appearance until the bleached material is disintegrated. At the back of the beater-roll a thin film may sometimes be seen on the surface of the water. This in time builds itself up on the sides of the beater. The characteristic sweetish odour of the isolated wax can be traced back often to the bleached material, which sometimes smells strongly.

I think there is evidence that this substance does does not exist in the raw fibre, but is formed in the cell wall during treatment. It is hardly probable that this substance, which is readily dissolved by soda, should survive the treatment with alkali under pressure. The odour which is characteristic of this substance is not noticed in the raw material until after the warm bleaching, and appears to be more developed after the bleached material is allowed to lie heaped up in a dense condition for some time. By altering the mode of bleaching of the raw materials, the occurrence of this waxy substance can be prevented. I found in one batch of cotton fibre, that smelt strongly of the waxy substance, that the alcoholic extract amounted to 2·87 per cent, and, when treated with ether afterwards, the ethereal extract amounted to 0·73 per cent.

The separation of the wax in the beater is merely a mechanical one, and is probably due to the fact that it intimately penetrates in the fibre. The knives of the beater-roll, which tear the ultimate fibre asunder, release the wax, which floats on the surface as a fine film, and quickly builds itself up on the metallic surface with which it comes in contact. I succeeded in at one time collecting about 50 lbs. of the deposit, which was found, on extraction with ether, to contain 77·54 per cent of wax.

4, New Court, Lincoln's Inn.

NITRO-CELLULOSE FILTERS.

By H. N. WARREN, Research Analyst.

THE above-named filters have been prepared and used by the author to great advantage during the examination of phosphates and other like precipitates, which always present more or less difficulty as regards incineration when in contact with carbonaceous substances. They are best prepared by the following means :—Chemically pure filter-papers that have been extracted with hydrofluoric acid, after having been thoroughly dried, are introduced, one at a time, into a mixture of equal parts by volume of nitric acid, 1·5 sp. gr., and good commercial oil of vitriol; each paper is allowed to remain for five minutes, and they are afterwards placed upon a sheet of glass, and washed with a full water supply until free from every trace of acid, the papers being afterwards carefully dried. They should be preserved in stoppered bottles, as they are slightly hygroscopic. By this means a paper is prepared corresponding to the formulæ of a trinitro-cellulose, burning almost instantaneously, and perfectly free from residue; these retain perfectly the finest precipitates, and at the same time filter much faster than ordinary papers. A paper possessed of slower combustion, and corresponding to dinitro-cellulose, may be obtained by using the ordinary nitric acid in admixture with twice its volume of vitriol; these, however, must not be brought in contact with ethereal solution, since dinitro-cellulose is readily soluble in that menstruum. A quicker and at the same time less expensive method may be employed, by using a mixture of one volume of ordinary nitric acid with two of vitriol, together with a small quantity of hydrofluoric acid ; into this mixture the ordinary cut filter circles may be introduced similar to the previous cases, the hydrofluoric acid at the same time removing the silica; papers thus treated showing a diameter of 5 inches, the ash of which amounted to 0·003 grm., showed after incineration a weight approximating to only 0·0025 grm.

The papers in either case, when containing precipitates, burn without any explosive violence, and are perfectly safe as regards projecting any substances they may contain.

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A NEW FLASK.

By HARRY M. SMITH.

IN the estimation of sugar by means of Pavy's solution it is very desirable to have a white background to the flask in which the titration is conducted. It occurred to me that the lower part of the flask might be made of white and opalescent glass. These flasks, as made for me by Mr. Müller, of 148, High Holborn, are about 2½ inches in diameter, and the lower third is almost porcelain-like in appearance. They give very satisfactory results, and, although specially designed for use in sugar analysis, they would, I think, be found useful in other processes where colour changes are concerned.

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SYNTHETIC EXPERIMENTS IN THE PYRAZOL SERIES.*

PART I.

By R. VON ROTHENBURG.

(Continued from p. 153).

On Alkylised Pyrazolons.

(3)-METHYLPYRAZOLON.—This substance was obtained at first from hydrazin and acetacetic ester, but afterwards from acetic anilide. The author has since obtained it by the action of hydrazinhydrate upon dehydracetic acid, tetrolic acid, β-isonitrosobutyric acid, or their esters and methyloxyazolon. In all cases the composition and the melting-point were correct.

(3)-Methyl-(4)-allylpyrazolon.—The allyl-group, on account of its non-saturated nature, might possibly have reacted with hydrazin hydrate and disturb the formation of pyrazolon. This conjecture proved to be unfounded. The compound forms leaflets melting at 195°. It is sparingly soluble in water, but abundantly in organic solvents, especially in heat. Its composition is $C_7H_{10}N_2O$.

(3)-Methyl-(4)-trimethylen-*o*-pyrazolon is formed from molecular quantities of hydrazin hydrate and acetyl-trimethylencarbonic ester. It crystallises from dilute alcohol in leaflets fusible at 197°. It is readily soluble in all solvents; it affords the characteristic reaction with ferric chloride, but does not react with diazo-salts or nitrous acid. Its composition is $C_6H_8N_2O$.

(3)-Phenylpyrazolon.—First obtained by Thun, at the instigation of Curtius, by condensing benzoyl acetester with hydrazin hydrate. It is fusible at 236°. The author has obtained a number of its derivatives.

Among the pyrazolons with condensed nuclei, the

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* From the *Journal Praktische Chemie.*

author describes (3, 4)-benzoisopyrazolon, discovered anhydride of ortho-hydrazinbenzoïc acid, which may be regarded as the quinoline of the pyrazolone series.

A condensation of pyrazolon itself with benzene is not conceivable, such as has become known in (4, 5)-benzopyridazolon. But the author has obtained the naphthaline of the pyrazolon series, *i.e.*

(3, 4)-Pyrazolono-pyrazolon.—If an excess of hydrazin hydrate is added to an alcoholic solution of (4)-isonitrosopyrazolon-(3)-carbonic acid it turns green and deposits a greenish grey precipitate, sparingly soluble in all solvents; it separates from dilute acids in white, granular crystals which are decomposed at 125—126°. The substance gives the characteristic reactions of pyrazolon. Its composition is $C_4H_2N_4O_2$.

It was not found practicable to arrive at (3)-bispyrazolon.

Hexahydrobenzo-(3, 4)-dipyrazolon was obtained by boiling an alcoholic solution of 1 mol. succinyl-succinic ester with hydrazin hydrate and acetate (2 mols.). It becomes an intense yellow with a blue fluorescence, and on cooling deposits a yellow granular powder. It is sparingly soluble in all solvents, and separates from hot dilute sulphuric acid in yellowish green and light brown prisms and needles fusible at 256—257°. It is a true pyrazolon derivative, coloured reddish yellow by nitrous acid and deep chestnut-brown with ferric chloride. Its composition is $C_8H_8N_4O_2$.

Hexahydrobenzodipyrazolone in an alkaline solution forms with the diazobenzene-salts a blood-red azo-compound.

Hexahydrobenzo-(4)-benzal-(3, 4)-dipyrazolon is formed by heating pyrazolon with its equivalent of benzaldehyd to 120—130°. It is practically insoluble in all solvents, and forms a reddish yellow granular powder quite unaffected by a temperature of 280°.

Hexahydrobenzo-(1, 1)-dimethyl-(3, 4)-dipyrazolon is formed by heating pyrazolon for some hours to 100° in a sealed tube with methyliodide and methyl-alcohol. Very sparingly soluble, yellowish, fusible above 250°. Reacts with nitrous acid with a red colouration.

Dihydrobenzo-(1, 1, 2, 2)-tetramethyl-(3, 4)-di-isopyrazolon is obtained from the foregoing on prolonged heating in a tube to 160—180° with a large excess of methyliodide and methylic alcohol, and can be freed from the accompanying impurities by its insolubility in alkalis and ammonia. More easily soluble than the foregoing. Does not react with nitrous acid and forms granular crystals fusible above 250°.

Hexahydrobenzo-(1, 1)-diacetyl-(3, 4)-dipyrazolon is formed on heating for a short time pyrazolon with 2 mols. acetic anhydride; a colourless granular powder fusible above 250°. It is soluble in alkalis. Its silver salt is sensitive to light, and it reacts with nitrous acid.

Dihydrobenzo-(1, 1, 2, 2)-tetracetyl-(3, 4)-di-isopyrazolon.—Is formed on submitting the former to a prolonged heat with an excess of acetic anhydride, and may be purified by its insolubility in alkalis and ammonia. It does not react with nitrous acid, and forms no silver salt. It is the most stable of its group, and crystallises from acetic ether or alcohol in globular aggregations, or white nodules, fusible above 250°.

The Constitution of the Pyrazolons. Isomerism and Tautomerism of the Pyrazolons. Course of the Reaction, and Conditions of the Formation of the Pyrazolons.

The somewhat considerable new material unfortunately does not admit of any remarkably enlarged insight into constitution of the pyrazolon ring. It must further be admitted that the constitutional determinations of Knorr have proved absolutely correct as against the objections of Nef.

So much is certain that pyrazolons and isopyrazolons are tautomerous and isomeric only in their isomers; that is, no isomers are capable of existence, the isomerism of which is occasioned solely by the position of the double bond in the nucleus. It must, however, be remarked that there is a second tautomerous form still more unstable than isopyrazolon, in the state of an (3)-oxypyrazol, and that its existence may be regarded as demonstrated, and that the following three configurations exist:—

I. Isopyrazolon. II. Isopyrazolon. III. (5)-Oxypyrazol.

A fourth conceivable form seems excluded on account of the entirely uniform behaviour of the derivatives of hydrazin hydrate and phenylhydrazin.

Only the form I. is capable of existence in the free state, II. in an acid, and III. in an alkaline solution, in which the pyrazolons behave exactly like phenols, *e.g.*, in the formation of azocompounds—a reaction which leaves nothing to be desired in point of complete analogy. In like manner, I am of opinion that the alkaline salts of acetaceticester contain the metal combined with oxygen, although I agree with Brühl and Von Pechmann in ascribing the ketone formula to the *β*-ketone esters. Whether we ascribe to the alkali-compounds the formula—

$$CH_3COAlc{:}C.HCO_2R,$$

or—

$$CH_3.CO.CH{=}C{<}\begin{matrix}O\ (Alc.)\\OR\end{matrix}$$

is quite non-essential for the formation of the azo-compounds, but I prefer the latter formula on account of its perfect analogy with the pyrazolons.

On the basis of the previous expositions, I must take up a sceptical attitude concerning the alleged discovery of isopyrazolon.

Such substances are capable of forming pyrazolons which contain a carboxyl-group (or a group equivalent in its stage of oxidation, *e.g.*, anilide, ester, &c.), and, in addition, in the *β*-position an aldehydic or ketonic-group, or a group which may re-generate an aldehydic or ketonic group or act as such (*β*-isonitrosopropionic acid = *β*-aldoximacetic acid) or in which the *α* and *β* atoms of carbon are connected by combination of acetylene (propiolic acids).

On Pyrazolidon.

As the three-fold non-saturated propiolic acid forms with hydrazin hydrate pyrazolon it might be expected that acrylic acid would yield pyrazolidon. The reaction agreed with the theory. Hydrazin hydrate reacts spontaneously with acrylic acid with an energetic liberation of heat. If heated it reacts with hydrazin acetate or tartrate. The solution, if it has an acid reaction, is neutralised with soda, shaken out with ether, and dried with calcium chloride.

On fractionation, the base boils at 133—135°, has a pungent odour like that of pyrazolon, mixes perfectly with ether, alcohol, &c., dissolves slightly in water, not in alkalis, easily soluble in acids; the specific gravity is smaller than that of water. Its composition is $C_3H_6N_2O$.

A characteristic of pyrazolidon is its behaviour with oxidising agents, which readily convert it into pyrazolidon, or the derivatives of the latter. It is purely a base: it does not dissolve in alkalis or in ammonia. It forms no silver salt, but at once reduces an ammoniacal solution of silver.

Pyrazolidon and Ferric Chloride.

Ferric chloride, if added in small proportion, colours the solution of pyrazolidon a violet red. The colour disappears on heating. On the addition of more ferric chloride, there appears the characteristic violet-brown colouration of the pyrazolons.

If pyrazolidon is treated at a boiling heat with the calculated quantity of a standardised solution of ferric chloride the solution becomes nearly colourless. The oxidation takes place almost quantitatively, if the iron is precipitated with alkali, and if paradiazotoluol sulphate is added with customary precaution.

Pyrazolon-(4)-*p*-azotoluol is precipitated in small red crystals, fusible at 219°.

It was not practicable to form an azo-compound of pyrazolidon, the result being merely a deep brownish red oil of an intense odour.

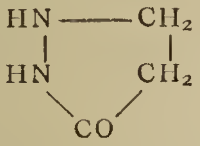
Pyrazolidon and Nitrous Acid.

Nitrous acid (as also bromine, mercuric oxide, silver oxide, lead peroxide, and similar agents) oxidise pyrazolidone to pyrazolon.

The original greenish colour depends, doubtless, on a true nitrosamine of pyrazolidon. We introduce nitrous acid until the solution takes a deep orange-yellow colour, neutralise cautiously with ammonia, and precipitate with silver nitrate pyrazolon-(4)-isonitroso-silver, which is then purified by re-solution in ammonia and cautious precipitation with acetic acid.

The Constitution of the Pyrazolidons. Isomerism and Tautomerism, Course of the Reaction and Conditions of the Formation of Pyrazolidon.

The pyrazolidons, as dihydropyrazolon, can only have the following constitution:—



The isomers can differ only in respect of the substituents, and phenomena of tautomerism do not occur; especially no hydroxyl-group can be formed, since these compounds are insoluble in alkalis and ammonia, form in alkaline solutions no azo-compounds, and are of a purely basic character.

As to the course of the reaction in the formation of pyrazolidon, it is not yet decided whether it is an additive process or the substitution process of a *β*-oxycarbonic acid formed intermediately.

The conditions of the formation of pyrazolidon are the presence of a carboxyl (or equivalent) group and fixation of ethylene between *α*- and *β*-carbon atoms, or *β*-hydroxyl in the nascent state.

(To be continued.)

ON THE

PREPARATION OF AMORPHOUS SILICON.

By M. VIGOUROUX.

The method generally taken for the preparation of amorphous silicon is that of Berzelius—reduction of the double silicon and potassium fluoride (fluosilicate) by potassium. The analysis proves that the silicon of Berzelius is far from pure.

H. Moissan having obtained pure amorphous boron by the reduction of boric acid in excess, by means of magnesium, we endeavoured to prepare amorphous silicon in the same manner, by heating silica with magnesium. Silicic acid being less readily fusible than boric acid, this preparation, which had been previously tried by several experimentalists, presented some difficulties.

In 1864 Phipson mentions the reductive action of magnesium upon silica. In 1867 Farkinson (? Parkinson) mentions the presence of magnesium silicide and silicate among the products of the reduction.

Gattermann (*Berichte*, xxii., p. 186) showed anew with what ease magnesium reduced silica, whether natural or artificial. On heating over a Bunsen burner he obtained a mass which, in hydrochloric acid, gave off a gas spontaneously inflammable, if the magnesium is in excess, and with the halogens formed silicon chloride, bromide, and iodide, if the silica is in excess.

Lastly, Winckler (*Berichte*, xxiii., p. 2642) endeavoured to prepare silicide of the formula Mg_2Si. He caused magnesium to act, firstly, upon silicon, and then upon silica. He pulverised two atoms of the metal with one of the oxide, and on heating only 0·20 grm. of this metal in a glass tube he experienced a violent explosion, the tube being shattered and the contents projected. If he operated in a current of hydrogen, the tube was not broken when he used 5 grms. or upwards of the mixture. There was formed a heterogeneous product, marked with blue and brown. On heating a mol. of silica with one of silicon, he did not obtain silicon protoxide. He infers that this latter compound does not exist.

We have sought for the conditions most favourable for the production of amorphous silicon, and, even when operating upon large quantitites, we were able to conclude—1st. That to avoid any explosion it is merely necessary to employ absolutely dry materials. 2nd. That if the mixture is very intimate the product is homogeneous.

Three series of experiments have been performed:—(*a*.) The proportion of magnesium was exactly necessary for the production of the silica with the formation of magnesia. After treatment there was obtained a powder of a chocolate colour in which were found silicides and numerous brilliant grains of silicon melted by the heat evolved at the moment of reduction; it is therefore requisite to moderate the reaction, (*b*.) We employed a variable excess of silica. There is formed less melted silicon, little or no magnesium silicide; but the treatments were very tedious and the yield always very slight. (*c*.) We operated in presence of magnesia. If we dilute the two active ingredients with this inert matter, the rise of temperature was much less. If we varied the proportions of magnesia, we were finally able to avoid the formation of melted silicon and that of magnesium silicide. We may then apply this result to the preparation of amorphous silicon.

To this end we take the proportions of magnesium and silica indicated by the formula—

$$SiO_2 + 2Mg = Si + 2MgO,$$

to which was added a quantity of magnesia equal to a fourth of their weight.

We used:—Silica, 180 grms.; magnesium, 144 grms.; magnesia, 81 grms. The silica selected was ground quartz met with in this state in trade. The magnesium was the powder employed for photographic purposes. The magnesia is the ordinary product, ignited strongly before the experiment. These three substances, mixed so as to form a very homogeneous powder, are poured into an earthen crucible holding double their bulk, covered with a layer of magnesia, and then dried as perfectly as possible.

When we wish to effect the reduction we introduce the crucible, still hot, into a Perrot furnace, previously heated to redness. In two or three minutes the reaction is set up. It is manifested by crackling, which lasted for some moments, and a bright incandescence of the entire mass; sometimes a little magnesium distilled and escaped between the crucible and the cover. In a minute afterwards the fire is extinguished, and the crucible withdrawn but kept closed. It is found that the material has increased in bulk, which shows the necessity of large crucibles.

The reaction takes place at 540°, measured by the thermo-electric forceps. This indication may be utilised whenever it is required to dry the product; it is sufficient to introduce the crucible when charged into the Perrot furnace kept at 300 or 400°. We may thus remedy the inconvenience of large crucibles, which do not easily find room in medium furnaces. It is sufficient to substitute for them smaller ones, each covered with a second crucible inverted and pierced at the base, which may project through the opening in the cover of the furnace. Thus most of the charges have been made in crucibles No. 14, fitted with a No. 12 crucible as a lid. It is necessary that the whole should be raised to the temperature of reduction. It may be produced by placing the mixture on a plate and covering it with magnesium powder. It is sufficient to apply a lighted match; the metal burns, and the heat evolved by the latter primes the reaction, which then continues spontaneously.

When cold it is a mass quite homogeneous, of a light maroon colour, without brown or blue marblings, porous and brittle, and easily detached. The inside of the crucibles has become a greyish blue, which shows that magnesium has exerted upon it a reductive action. If we wish to avoid this inconvenience the interior of the crucibles must be lined with magnesia, or the portions which have been in contact with the sides are rejected.

The powder is at first treated with hydrochloric acid. If the mixture was sufficiently intimate there is not a trace of hydrogen silicide, showing that no magnesium silicide has been formed. Boiling sulphuric acid removes the last traces of magnesium free or combined. Then, by two or three alternate treatments with hydrofluoric acid in the water-bath and with boiling sulphuric acid, the silica and the silicides can be removed. The process is completed with ebullition in hydrochloric acid, and then in water.

After desiccation we obtain a powder of a maroon colour, perfectly homogeneous.

If chemically pure materials are employed, we obtain a silicon containing 99·09 to 99·69 per cent; with commercial products the figures are not very different.—*Comptes Rendus*, cxx., p. 94.

THE CHEMOMETER.[*]

By W. OSTWALD.

(Continued from p. 154).

On the basis of Faraday's law it is now possible to conduct the processes between electrolytes so that they cannot take place without a simultaneous movement of electricity, and that the quantities of work which may be obtained from the chemical process may be manifested in the form of electrical energy. As, on the one hand, the electrical energy is equal to the chemical, and, on the other, the factors of capacity on either hand, the quantities of matter, and the quantities of electricity are proportional according to Faraday's law, the magnitudes of intensity, the chemical potential, and the electromotive force are proportional to each other, and the electrometer serves as a chemometer in the sense above expounded. And as electromotive forces can be distinguished only by number and sign, we have a universal measure of the chemical potential, or, as we may justly name this magnitude, of the chemical affinity.

In order to illustrate the result of an example, we may take any single chemical reaction, *e.g.*, the precipitation of silver nitrate by sodium chloride. In order to utilise this process electro-chemically we must resolve it into two parts, which certainly occur simultaneously but separate in space, as we otherwise could not transform the chemical energy into electrical, but should obtain it as heat. We obtain this if we take two silver plates, placing the one in the solution of silver nitrate, and the other in that of sodium chloride. If both solutions are connected by an indifferent electrolyte, the two silver plates show a very distinct difference of potential of rather more than 0·3 volt; and if we set up the current by means of a conductive connection of both plates, silver chloride is formed on the plate immersed in sodium chloride, whilst metallic silver is deposited on the other plate. The total quantity of metallic silver remains therefore unchanged; a certain quantity of silver nitrate has disappeared; on the other hand, an equivalent quantity of silver chloride is formed: finally, the NO_3 ions of the silver nitrate and the Na ions of the sodium chloride have travelled into the intermediate vessel and have formed sodium nitrate. The chemical result of the total process is exactly the same as if sodium chloride is directly added to the solution of silver nitrate.

In a similar manner all chemical processes between electrolytes may be transformed into voltaic chains, care being only taken that the chemical process cannot take place without the electrical. Thus much trouble has been taken concerning the chain formed by one of the most important processes—the neutralisation of an acid by a base. Such a one is obtained if we plunge, both into the acid and the alkali, a plate of platinum or palladium saturated with hydrogen. On suitable connection there is then, on the side of the alkali, an absorption of hydrogen, whilst on the side of the acid there ensues an equal liberation of hydrogen. At the same time the current between the solutions, the basic kathions, and the acid anions, are moved towards each other in corresponding numbers, and thus neutralised. The electromotive force of neutralisation is about $\frac{3}{4}$ volt for powerful acids and bases, and for weaker ones is of course smaller.

It would take us too far if I were to explain only all the typical cases of the possible reactions between acids, bases, and salts. The remark must suffice that it is always practicable, and that for each such reaction we obtain the accompanying electromotive power.

A further remark must be made. The electromotive power of the circuits described is essentially composed of two items, the potential differences which exist at each electrode in respect to the liquid. We do not therefore require a direct measurement of all combinations, but may be content with determining all the combinations with one electrode, in order if we have, *e.g.*, twenty different substances, to calculate the electromotive forces of all the two hundred combinations which are possible between them all.

Thus the problem of the chemometer is solved for electrolytes.

Considering the importance of the result and the general character of the duction employed, it may be useful to show the accuracy of the result in another manner. To this end I will make use of a form of the second main theorem of energetics, which, although it has been used in principle by Lord Kelvin years ago, has only been lately expressed in general terms. The theorem is—Whatever is in equilibrium in any manner must be in equilibrium in every manner, and its proof lies in the truth that whenever it is not fulfilled it is possible to construct a *perpetuum mobile* of the second kind, a combination in which quiescent energy sets itself spontaneously in motion, which according to experience is impossible.

If we now suppose two substances in chemical equilibrium, which we arrange in a suitable manner, but showing an electrical difference or an electromotive power; then let the current be set up and any machine be driven by its means, until an electrical equilibrium is produced in consequence of the chemical changes accompanying the current; the existing chemical equilibrium must then be disturbed, but we can restore it by the interaction of the substances. The conditions are then given for obtaining electric work anew, and so on. The same series of inferences holds good if we begin with the assumption that the substances are in electrical but not chemical equilibrium.

Chemical and electrical equilibrium must therefore be simultaneously present. If the former is wanting, the latter cannot exist. Both deviations must take place in such a manner that the chemical processes depending on the electromotive force are engaged in an approximation to equilibrium.

(To be continued).

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[*] From the *Zeitschrift fur Physikalische Chemie.*

IS ARGON CONTAINED IN VEGETABLE OR ANIMAL SUBSTANCES?*

By GEORGE MACDONALD, B.Sc., and ALEX. M. KELLAS, B.Sc.

At Professor Ramsay's suggestion, experiments were undertaken to see whether argon could be obtained from nitrogenous vegetables or from animal tissues.

Method:—A few grms. of the substance, after drying if necessary, were ground to a fine powder, desiccated at 110° C., until the weight was constant, and a nitrogen estimation performed by Dumas's method. It was supposed that any argon compound would be decomposed, when the argon would come off along with the nitrogen. The gas was collected in a nitrometer over well-boiled concentrated potash solution, whence it was transferred to a small gasholder containing water which had been boiled for some hours. The gasholder was connected with an apparatus similar in general arrangement to that used by Prof. Ramsay in July last, which enabled the gas to be dried and purified from hydrocarbons, carbon monoxide, or hydrogen, the nitrogen being absorbed by being passed and re-passed over magnesium turnings kept at a temperature of about 600° C. A three-way stopcock enabled the magnesium tube and the purifying and drying tubes adjoining it to be connected either with the second gasholder or with a "Sprengel," so that any residual gas could be pumped off, and the tubes exhausted before admitting the gas. The gas pumped off was collected in a piece of hard glass tubing; it was then mixed with oxygen prepared by heating potassium permanganate, and sparked down until no further diminution of volume occurred, when excess of oxygen was known to be present. The remaining gas was transferred by a gas pipette to a tube standing over mercury, and the oxygen present absorbed by potassium pyrogallate solution. Only one experiment was carried through to the end in each case as the results seemed conclusive, although several determinations of nitrogen were made.

Peas were selected as a typical vegetable, and the following is a summary of the results:—

Expt.	Weight of Desiccated Peas taken.	Volume of Nitrogen collected (corrected for temp. and press).	Weight of Nitrogen.	Percentage of Nitrogen in Dried Peas.
	Grms.	C.c.	Grm.	
1	8·9446	465·8	0·5843	6·53
2	8·9455	466·8	0·5856	6·55
3				

342 c.c. of the volume collected in the first experiment (which was done in two parts) was passed over the heated magnesium until so much nitrogen was absorbed that both gasholders were full of water, and the residue was then left for about twelve minutes in the tubes, the magnesium being kept heated so that absorption of nitrogen might continue. On connecting with the pump a pressure of about 2 inches was registered, and the volume of gas pumped off had a volume of nearly 8 c.c. After sparking down with excess of oxygen, 6·8 c.c. of gas was left, and on absorbing by a strong solution of potassium pyrogallate (stronger than Hempel recommends for complete absorption) 0·12 c.c. of gas remained, which is less than 0·04 per cent of the volume taken. To see if this bubble of gas consisted of carbon monoxide, two experiments were performed with the oxygen used: 9 c.c. gave 0·2 c.c. residue, and 11·2 c.c. gave 0·25 c.c. residue, with about the same strength of pyrogallate.

As the quantity of oxygen used in sparking down was over 20 c.c., it might safely be concluded that there is no appreciable quantity of argon in peas (or at least that the argon cannot be obtained with the nitrogen by Dumas' method).

The experiment with regard to the presence of argon in animal tissues was also negative in its results. Mice were selected for the experiment, because the nitrogen from the whole animal could be conveniently collected by Dumas' method. The crucial experiment was carried out in the same way as before.

From three mice 550 c.c. of nitrogen was obtained. This was absorbed by heated magnesium as usual, but the residual gas was left for over an hour in the tubes after the gasholders had been emptied, so that on connecting up with the pump only a few m.m. of pressure was registered, and the total gas pumped off occupied about 1 c.c. After sparking down with large excess of oxygen about 10 c.c. remained, which gave a residue of 0·2 c.c. with alkaline pyrogallate, which would be about 0·36 per cent of the volume taken.

Very careful experiments were undertaken to determine the exact percentage of nitrogen contained in mice, as the volume from the first experiments seemed too high. Two experiments with complete mice gave the following results:—

	Weight of Mouse.	Percentage of Water lost at 110° C.	Percentage of Nitrogen in Desiccated Animal.
	Grms.		
A	13·7	73·1	11·0
B	12·5	70·5	10·6

A Kjeldhal determination of the nitrogen in a small quantity of mouse A, by Mr. Frye, gave 9·6 per cent, so that the high percentage seems confirmed.

A POSSIBLE EXPLANATION OF THE TWO-FOLD SPECTRA OF OXYGEN AND NITROGEN.*

By E. C. C. BALY, A.I.C.,
1851 Exhibition Scholar in University College, London.

The two spectra of oxygen are shown to be of a different nature. They behave differently, and reasons are given for their being in all probability the spectra of different gases. They may either be two spectra produced by different vibrations of the oxygen molecule, or they may be the spectra of two different modifications of oxygen, or the spectra of two distinct gases resulting from a dissociation of oxygen, a combination of which is called oxygen.

It appeared worth while to undertake experiments with a view of testing the last of these. Oxygen was sparked in an apparatus similar to that used by Prof. J. J. Thomson in his experiments on the electrolysis of steam. Hollow platinum electrodes were used, each one of which was connected with a Sprengel mercury pump. In the first experiments the distance between the electrodes was 35 m.m, and the highest pressure compatible with the appearance of the two spectra was made the starting-point of the experiments. In these first experiments it was 380 m.m. The density of the oxygen before sparking was determined, and taken as a test of its purity. The fractions obtained from the anode and cathode were weighed, and the results are given. They follow the lines of J. J. Thomson's results, inasmuch as with long sparks a lighter fraction was obtained at the cathode, and with short sparks a heavier fraction. The fractions from the anode were not so definite as from the cathode, though the difference was in the right direction. The probable maximum error of weighing was 0·0001 grm. This meant exactly one in the second decimal place of the density obtained. The general accuracy of the results may be gauged from the densities of unsparked oxygen obtained.

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* A Paper read before the Royal Society.

* Abstract of a Paper read before the Roal Society.

Density of Cathode Fraction with Long Sparks.	Density of Oxygen Unsparked.	Density of Cathode Fraction with Short Sparks.
15·78	15·88	16·00
15·79	15·87	16·01
15·80	15·89	16·02
15·79	15·88	16·04
	15·88	16·06
		16·05

Mean of results of other observers = 15·887.

Density of cathode fraction from oxygen, previously for three days fractionated with short sparks, 15·75.

The experiments are still in progress.

A RE-DETERMINATION OF THE ATOMIC WEIGHT OF YTTRIUM.[*]

By HARRY C. JONES.

(Concluded from p. 157).

II. *Conversion of the Sulphate into Oxide.*

Yttrium sulphate was prepared by dissolving the oxide in dilute sulphuric acid and evaporating the solution to a small volume on the water-bath, when the sulphate crystallised out. The mother-liquor was then poured off, and the sulphate dried by pressing between filter-paper. The desired amount of the sulphate was placed in the platinum crucible, which had been heated over the blast-lamp to constant weight, and itself dried to constant weight in the cylindrical air-bath previously described, at a temperature a little above the boiling-point of sulphuric acid. The weighed sulphate was then decomposed to the oxide in the platinum crucible over the blast-lamp. During the latter part of the heating the lid was removed from the crucible, and the oxide heated in direct contact with the air.

The heating was continued until the oxide had attained a constant weight, and the oxide was tested in every case for the presence of sulphate. When constant weight was reached under the conditions employed, every trace of sulphate had been decomposed to oxide.

To test the reliability of this method a weighed amount of yttrium oxide was converted into sulphate by the method first described, and then this sulphate decomposed to oxide by the method just described. If the method of decomposition of the sulphate was trustworthy, then the same amount of yttrium oxide should have resulted from the decomposition of the sulphate as was originally used. Two such tests were made, and in both cases the amount of oxide obtained from the sulphate agreed with the amount originally used to within a tenth of a m.grm.

Below are the results of the ten determinations by this method, which were finished satisfactorily. Here also an occasional determination was lost by accident.

	$Y_2(SO_4)_3$.	Y_2O_3.	$3(SO_3)$.	$\left\{\begin{array}{l} O=16 \\ S=32·06 \end{array}\right\}$ At. wt. yttrium.
I.	0·5906	0·2862	0·3044	88·91
II.	0·4918	0·2383	0·2535	88·89
III.	0·5579	0·2705	0·2874	89·03
IV.	0·6430	0·3117	0·3313	88·99
V.	0 6953	0·3369	0·3584	88·89
VI.	1·4192	0·6880	0·7312	88·99
VII.	0·8307	0·4027	0·4280	88·99
VIII.	0·7980	0 3869	0·4111	89·02
IX.	0·8538	0·4139	0·4399	88·99
X.	1·1890	0·5763	0 6127	88 96
Total	8·0693	3·9114	4·1579	
Average				88·97

The mean atomic weight from the ten determinations is 88·97, the highest value found being 89·03, the lowest 88·89. The atomic weight of yttrium calculated from the total sulphate, 8·0693 grms., and the total oxide, 3·9114 grms., is 88·97.

The agreement between the two series of determinations is satisfactory, and the atomic weight of yttrium, as determined from the oxide which I employed, is about 88·95.

Historical Sketch.

To show how widely the results of the different determinations of the atomic weight of yttrium which have been made differ from one another. I give the following brief sketch:—

The earliest determination was made by Berzelius (*Schweigg. J.*, xxii., 336; xvi., 422; *Pogg. Ann.*, viii., 186) in 1818. From his analysis of the carbonate. Ostwald ("Lehrbuch zweite Auflage," Bd. i., 122) has calculated the atomic weight Y = 105. Meyer and Seubert ("Atomgewichte der Elemente"), from Berzelius's analysis of the sulphate, have calculated the atomic weight Y = 96·77. (O = 16.)

From the analysis of the sulphate made by Popp, 1864 (*Liebig, Ann. Chem.*, cxxxi., 191), Ostwald has calculated the atomic weight Y = 102·13. From Popp's determination of yttrium in the sulphate, by precipitation as oxalate and weighing as oxide, Meyer and Seubert have found the atomic weight Y = 101·90. (O = 16)

From the determinations of water in the sulphate, made by Delafontaine, 1865 (*Liebig, Ann. Chem.*, cxxxiv., 109), Meyer and Seubert have found the atomic weight Y = 97·86. (O = 16.) From his determinations of yttrium in the sulphate they calculate Y = 96·64. (O = 16.)

Bahr and Bunsen, 1866 (*Liebig, Ann. Chem.*, cxxxvii., 21), dissolved yttrium oxide in sulphuric acid, evaporated on the water-bath, and gradually heated above the boiling-point of sulphuric acid. From the results Meyer and Seubert give Y = 92·80. (O = 16.) Pure oxide was transformed into basic nitrate, and in this way was found Y = 92·48.

The above determinations are now only of historic interest, since, in the light of more recent discoveries, it is almost certain that in each case mixtures of yttrium wsth other rare earths, some of which were known and others not suspected, were employed.

Clève and Höglund, 1873 (*Bihang. till. Vet. Aks. Handl.*, 1873, i., iii., No, 8), seem to have had the purest material up to their time. By converting the oxide into the sulphate they found Y = 89·58. (O = 16, S = 32·06).

Clève, 1883 (*Bull. Soc. Chim.*, xxxix., 120) converted as pure yttria as could be obtained into the nitrate, and repeatedly fractioned by means of oxalic acid. Finally he obtained a small quantity of yttria whose molecular weight remained constant. This was separated by means of oxalic acid into four fractions, each of which gave a sulphate containing about the same quantity of yttria. 23·2091 grms. of the sulphate gave 11·2568 grms. of the oxide. From this follows Y = 89·1. (O = 16, S = 32·06.)

There seems to be no doubt that Clève's yttria was the purest hitherto employed, and his determination has, up to the present, been justly regarded as nearest to the true atomic weight of the element.

The value which I have found is about 0·15 of a unit lower than that of Clève, which argues for a corresponding increase in purity in my material over that of Clève's, since the impurities commonly present have a higher atomic weight than yttrium. The impurity in the oxide which I used, which from spectrum analysis cannot exceed ½ per cent, and is probably less according to Rowland, is very likely a remnant of the "erbium" group which was not completely separated by the potassium ferrocyanide. The true atomic weight of the element yttrium is then, in all probability, a little lower than 88·95, the value found from the yttria which I employed.

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[*] *American Chemical Journal*, vol. xvii., No. 3.

Crookes (CHEM. NEWS, lxx., 81) has recently raised the question as to whether the atomic weight of the yttrium obtained by Rowland had been determined. The work described in this paper, which was carried out before Crookes's communication was seen, will, it is hoped, answer that question satisfactorily.

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.†

By AMOS PEASLEE BROWN.

(Continued from p. 155).

I. *Table Showing Average Relative Oxidation of Sulphur in Pyrite and Marcasite by Solutions of* $KMnO_4$ *at 22° and at* 100°. (See Pl. xvii.).

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.	On Pl.
Pyrite $\frac{1}{100}$ N. cold	·78	1·17	1·38	1·74	1·72	22° P_1
Marcasite $\frac{1}{100}$ N. cold	1·07	1·86	2·04	(1·25)	2·38	22° M_1
Pyrite 1 per cent cold	1·71	(1·43)	1·86	1·85	1·80	22° P_2
Marcasite 1 per cent cold	1·22	1·21	2 06*	2·32*	2·24	22° M_2
Pyrite 3 per cent cold	2·55	2·27	2·80*	2·55	2·55	22° P_3
Marcasite 3 per cent cold	2·80	2·25	2·87*	2·88*	2·80	22° M_3
Pyrite 5 per cent cold	2·77	3·09	2·77	2·89	3·02	22° P_4
Marcasite 5 per cent cold	2·31	3·41	3 30*	3·16	3·78	22° M_4
Pyrite $\frac{1}{100}$ N. 100°	4·05	4·72	3·36	2·04	5·64	100° P_1
Marcasite $\frac{1}{100}$ N. 100°	3·17	3·84	3·76	5·63	5·61	100° M_1
Pyrite 1 per cent 100°	6·03	6·98	8·38	6·11	6·88	100° P_2
Marcasite 1 per cent 100°	6·43	5·93	8·56	7·40	9·10	100° M_2
Pyrite 3 per cent 100°	6·26	6·83	6·81*	10·73	11·08	100° P_3
Marcasite 3 per cent 100°	6·47	7·97	9·42	9·80	(7·55)	100° M_3
Pyrite 5 per cent 100°	7·95	7·52	9·85	11·86	14·98	100° P_4
Marcasite 5 per cent 100°	8·38	8·38	13·27	14·85	16·36	100° M_4

* Obtained by omitting discordant results.

II. *Table Showing Selected Results of the Oxidation of Sulphur in Pyrite and Marcasite by Solutions of* $KMnO_4$ *at 22°.* (See Pl. xviii.).

Mineral.	One-hour.	Two-hour.	Three-hour.	Four-hour.	Five-hour.	On Pl.
Pyrite $\frac{1}{100}$ N. cold	·78	1·17	1·38	1·74	(1·72)	22° P_1
Marcasite $\frac{1}{100}$ N. cold	1·07	1·86	2·04	(1·25)	2·38	22° M_1
Pyrite 1 per cent cold	(1·71)	1·47	1·85	1·90	1·89	22° P_2
Marcasite 1 per cent cold	1·16	1·29	1·93	1·95	2·15	22° M_2
Pyrite 3 per cent cold	(1·65)	2·31	2·80	(2·62)	2·81	22° P_3
Marcasite 3 per cent cold	(2·72)	2·33	2·87	2·88	2·83	22° M_3
Pyrite 5 per cent cold	2·39	3·03	3·22	(2·89)	3·24	22° P_4
Marcasite 5 per cent cold	2·52	3·06	3·82	(3·16)	4·17	22° M_4

No very marked difference in the rate of oxidation is brought out by this series of experiments, the amount of sulphur oxidised never having reached the critical point in pyrite, as shown by Prof. Smith's oxidations with the current already described. This point at which the rate of oxidation of sulphur in pyrite suffers a change was found by Prof. Smith to be between 21 and 22 per cent from the results of a very large series of current oxidations.* The explanation for this being the critical point in the oxidation of pyrite will be given in the discussion of its constitution. The experiments with permanganate oxidation simply show then that up to near this point (the highest point reached in the pyrite oxidation was nearly 15 per cent) the relative rates of oxidation of the two minerals do not differ widely from each other, but that marcasite oxidises somewhat faster than pyrite. This is simply what has long been known and recognised in regard to atmospheric weathering.

As will be seen when the constitution of these minerals is considered, marcasite cannot have a critical point in regard to oxidation of its sulphur.

The experiments thus far described had for their object the removal of sulphur. On the other hand, a number of ways of attacking the iron were tried and with more interesting results. In these trials reagents were selected which would attack the iron more energetically than the sulphur. Among these may be classed the experiments of solubility in acids.

Hydrochloric acid (hot or cold, concentrated or dilute) has little action on these minerals. Pyrite was treated for one hour with boiling concentrated HCl, of specific gravity 1·20 in covered beakers, and showed in the solution only 2·56 per cent of iron out of 46·67 per cent. Marcasite, treated in the same way, gave an identical result. Similar experiments at the ordinary temperature were tried with both minerals, by digesting for three days with excess of concentrated hydrochloric acid and with excess of $2HCl+3H_2O$, but even after three days the action was very slight in both cases. Pyrite gave with both concentrated and dilute acid the same result—a solution of 1·51 per cent of iron. Marcasite gave almost identical results. The concentrated hydrochloric acid solution showed 1·51 per cent of iron, the dilute solution 1·89 per cent. No evolution of hydrogen sulphide was detected by lead paper in either case. Concentrated sulphuric acid at boiling temperature decomposes both minerals, with evolution of sulphur dioxide and the separation of sulphur, but the action is very slow and seems to take place more readily with pyrite than with marcasite. Pyrite digested with concentrated sulphuric acid at boiling temperature for one hour showed 14·81 per cent of the iron dissolved, but marcasite under like conditions was only attacked in one hour to the extent of 12·77 per cent of iron. Trials were also made in the cold, but did not differ materially from the results obtained with HCl.

More important results were obtained by conducting dried hydrochloric acid gas over the minerals at an elevated temperature. In these trials 0·2 grm. of the mineral was placed in a porcelain boat and heated in a glass tube in a strong stream of the gas. The sulphur in the series of experiments at the lower temperature was collected by passing the gas through bulbs containing $Br+HCl$; at the higher temperatures, the residue in the boat was analysed and the sulphur lost estimated by difference. In the experiments at low temperature the entire tube was exposed to a temperature of 210°, as determined by thermometer. The HCl was passed over in a strong stream for one hour. The action at this temperature was slight; the results obtained do not, however, show the entire amount of sulphur removed, as some remained in the cool end of the tube, from the dis-

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† Read before the American Philosophical Society, May 18, 1894.—From the *Proceedings of the American Philosophical Society*, xxxiii., No. 145.

* Private communication from Prof. E. F. Smith, 1893.

sociation of the hydrogen sulphide. As the action was so slight, no attempt was made to collect and estimate this sulphur remaining in the tube. In the bromine and hydrochloric acid solution was found sulphur as follows:—

Pyrite at 210° in current of HCl (*a*)	0·94
,, ,, ,, ,, (*b*)	0·93
Marcasite at 210° in current of HCl (*a*)	0·77
,, ,, ,, ,, (*b*)	0·59

More marked results were obtained by increasing the temperature. Similarly conducted experiments were carried out at 310° and 325°, the time of heating ranging from one to three and one-half hours. The temperature of 310° was graded by keeping it between the melting points of $NaHSO_4 H_2O$ (300°) and $NaNO_3$ (313°), the higher temperature was between the last 313° and the melting point of $KClO_3$ (334°). After the HCl had been passed for a sufficient length of time, the tube was allowed to cool (with the gas current continued until cold) and then the remaining sulphur estimated by oxidising the contents of the boat with nitric acid and potassium chlorate and precipitating and weighing as $BaSO_4$. The amount found, subtracted from 53·33 per cent, gave the loss of sulphur. In this case the results obtained by oxidation were reversed, the pyrite lost more sulphur than the marcasite. This is an expression of the fact that the hydrochloric acid gas (or its contained Cl) acts more vigorously on the iron of pyrite than on that of marcasite. The results of the reaction were in each case ferrous chloride in the boat and free sulphur in the tube, the latter from dissociation of the hydrogen sulphide. No ferric chloride was seen in the tube, except a trace with the pyrite. Each mineral was heated for one hour at 310° in a current of the gas and showed loss of sulphur as follows:—

Pyrite heated at 310° for one hour in HCl, sulphur lost	10·73
Marcasite heated at 310° for one hour in HCl, sulphur lost	7·19

About the same relative amounts were lost on heating for three and one-half hours at 325°. The results thus obtained were as follows:—

Pyrite heated at 325° for three and one-half hours in HCl, sulphur lost	17·13
Marcasite heated at 325° for three and one-half hours in HCl, sulphur lost	10·70

Besides these two experiments, pyrite was heated for one hour at a red heat in a stream of the gas. A copious sublimate of ferrous chloride was found in the tube, with a trace of ferric chloride and sulphur. This time the loss was 46·47 per cent of sulphur. It seems evident from these experiments that, as above stated, the iron in pyrite is in a condition that is more readily acted on by hydrochloric acid than is the iron in marcasite. It will be proved that the iron in marcasite is all ferrous, while part of that in pyrite is ferric, and this is probably the explanation of the above phenomenon. All of the iron in each case described above would form ferrous chloride ($FeCl_2$) on account of the reducing action of the hydrogen sulphide formed. Under the conditions of the above experiments, the critical point developed in the oxidation of pyrite was not reached, but it is not likely that it exists with this reagent, or if there be a critical point it is not 21 per cent. The thought suggested itself to me that perhaps some sulphur would be lost in pyrite if it were heated to 325° in a neutral atmosphere, and that this might account for the difference shown in the loss of sulphur in the two minerals. This proved not to be the case. Pyrite heated in this way in an atmosphere of nitrogen gave no appreciable loss after one hour at a temperature of 325°.

Instead of hydrochloric acid gas, the action was tried of ammonium chloride at temperatures up to 335° and in an atmosphere of nitrogen. Under these conditions the sulphur was combined as ammonium sulphide probably and did not exert such a reducing action on the iron. These experiments were conducted as follows:—0·2 grm. of the finely pulverised mineral was mixed with 0·5 grm. dry ammonium chloride and introduced (in a porcelain boat) into a glass tube. Test samples of $NaHSO_4.H_2O$ and $KClO_3$ in sealed tubes were used to regulate the temperature. All air was displaced in the tube by nitrogen and a slow current of nitrogen passed through the tube before heating. Under these conditions with marcasite, sulphur ammonium sulphide were found sublimed in the tube along with ammonium chloride, and in the boat there was found much ferrous chloride without any ferric chloride, but in the case of the pyrite there was formed a large proportion of ferric chloride, which sublimed on the tube towards the end of the operation. The heating was conducted slowly in each case and continued until all ammonium chloride was sublimed from the boat, the temperature of 335° not being exceeded during this time. The entire operation lasted about twenty-five minutes in each case. Three trials of each mineral were made and with the same result in each case; with marcasite only ferrous chloride was found in the boat and no iron in the tube, pyrite always gave much ferric chloride and little ferrous. The amounts of sulphur removed are probably not very significant; they showed the following results:—

Pyrite heated with NH_4Cl lost sulphur (*a*)	7·02
,, ,, ,, ,, (*b*)	7·10
Marcasite ,, ,, ,, (*a*)	9·50

(To be continued).

CORRESPONDENCE.

THIO-ACETIC ACID.

To the Editor of the Chemical News.

Sir,—Being interested in the discovery by Messrs. Schiff and Tarugi of the use of ammonium thio-acetate as a substitute for sulphuretted hydrogen, which was described in your columns a few weeks back, I made a quantity of that reagent according to their directions, and noticed the following peculiarities not mentioned in the paper by the authors:—

That the precipitate of cadmium sulphide, obtained by the use of this reagent, instead of being yellow, is of a reddish colour, and might easily be mistaken for antimony.

Stannic salts produced a brown-black precipitate of stannous sulphide, instead of the usual yellow stannic sulphide.

And, lastly, having left about 100 c.c. in a tight-stoppered flask, on returning to it after a few days I found the flask had been burst, presumably by the accumulation of gas generated from the reagent.

The thio-acetic acid was made as usual by distilling glacial acetic acid with phosphorus pentasulphide, and it was dissolved in ammonia without being purified by redistillation.

I should like to know if anyone else has noticed these peculiarities, and also if anyone could explain the cause of the one last mentioned.—I am, &c.,

Fredk. Soddy.

The Laboratory,
University College, Aberystwyth.

Appointment.—Dr. A. W. Crossley, Ph.D. (Würzburg), M.Sc. (Victoria), Berkeley Fellow and Demonstrator of Organic Chemistry in the Owens College, Manchester, has been elected Demonstrator of Chemistry in the Medical School of St. Thomas's Hospital in succession to Dr. W. H. Ince, who has been appointed Government Chemist at Trinidad.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 11, March 18, 1895.

Attempts to Cause Argon to Enter into Chemical Combination.—M. Berthelot.—Already inserted.

Nomination.—The Academy proceeded to the nomination of a free member, *vice* the late F. de Lesseps. M. Carnot was elected, having obtained an absolute majority of votes.

Transformations of Fibrine of the Prolonged Action of Weak Saline Solutions.—A. Dastre.—The solution upon which the author was experimenting contained a fibro-globuline α, analogous to fibrinogene, coagulable at 55°; a fibro-globuline β, coagulating above 75°; certain peptones or proteoses giving the reactions of the proteoses of gastric digestion, and traces of peptones. With chlorides and iodides the action is as energetic in weak as in strong solutions. With fluorides at 5 per cent the reaction is minimal or null.

Action of Nitrous Oxide on Metals and Metallic Oxides.—Paul Sabatier and J. B. Senderens.—The oxidising action of N_2O upon metals and their oxides is very imperfectly known. It is known that potassium and sodium if slightly heated in this gas burn vividly, and that iron, manganese, zinc, and tin, if heated to redness, are oxidised more or less quickly. The gas, carefully purified and dried, was passed over the substances in question at temperatures always below 500°. Cadmium heated to near the melting-point, 320°, is gradually oxidised and volatilised, forming a brown deposit of oxide on the sides of the tube. Lead, obtained in a state of fine division on reducing litharge by hydrogen, is slowly oxidised about 300°, and reproduces yellow litharge. Iron, reduced at redness in a prolonged current of hydrogen, burns below 170°, forming red ferric oxide. Reduced cobalt burns incompletely about 230°, being re-converted into brown cobaltous oxide (cobalt 82·1 per cent). Nickel, reduced, is oxidised with incandescence at 300°, forming monoxide. Reduced copper remains unchanged at 200°, but above 250° it is slowly transformed into red cuprous oxide. Near dull redness we may obtain a slight incandescence. *Lower Oxides.*—Greenish yellow manganous oxide, obtained by reducing the sesquioxide, is oxidised with incandescence about 350°, and forms light brown Mn_3O_4. Tungsten bioxide, WO_2, of a blackish brown colour, is transformed without incandescence at 450° to the blue oxide, WO_2, not mixed with tungstic anhydride. Molybdenum sesquioxide, Mo_2O_3, is slowly changed into the violet oxide, MoO_2. Brown stannous oxide, SnO, burns at 400°, forming white stannic oxide, SnO_2. Purple cuprous oxide, Cu_2O, prepared previously, is not oxidised at 350° in nitrous oxide; its weight remaining identical. Black vanadium sesquioxide, prepared by reducing with hydrogen vanadic anhydride, Va_2O_5, is not modified below 500°. Yellow uranium oxide reduced in hydrogen at bright redness, forms uranous oxide, of a maroon brown, which is not altered by nitrous oxide at 450°. If the reduction is effected at a lower temperature the uranous oxide is black and burns in nitrous oxide at about 400°, forming black oxide, U_2O_5.

The Combination-Heats of Mercury with the Elements.—Raoul Varet.—A thermo chemical paper not adapted for useful abstraction.

Isomeric States of Mercury Oxides.—Raoul Varet.—Like the iodides, the mercury oxides assume a red and a yellow state; both stable in the cold, and thus differing from the iodides. The conversion of the yellow mercury oxide into the red state gives rise to no appreciable thermic effect. This explains why the red and the yellow varieties are equally stable at ordinary temperatures. As to the two iodides, the transformation of the yellow into the red state is accompanied with a liberation of heat of +3 cal. The more exothermic compound only is stable in the cold.

Formation-Heat of some Compounds of Iron.—H. Le Chatelier.

On the Chloroaldehyds.—Paul Rivals.

Crystalline Isomer of Monochloroaldehyd.—Paul Rivals.—These three thermo-chemical papers do not admit of ready abstraction, and cannot claim insertion in full.

Mercuric Compound of Thiophene permitting its Separation and Determination in Commercial Benzenes.—G. Deniges.—The author has endeavoured to isolate thiophene in the form of an insoluble compound, and the presence of sulphur in its mol. led him to employ for this purpose the salts of mercury, the affinity of which for organic sulphur compounds is well known. The author proposes to develop his procedure in a future paper.

The Amorphous State of Melted Bodies.—C. Tanret.—The author studies the state of substances originally crystalline, but rendered amorphous by fusion.

Derivatives of Active α-Oxybutyric Acid. (1. Butanoloïc Acid).—Ph. A. Guye and Ch. Jordan.—The authors have split up racemic oxybutyric acid into its two optical isomers, and have undertaken the study of its principal active ethers.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 1, 1895.

Rotatory Power of some Ethers of β-Methyladipic Acid.—P. Freundler.—Methyladipic acid crystallises in white tablets fusible at 91—92°. It distils unaltered at 211° (at a pressure of 15 m.m.). Its specific rotatory power at 2 per cent in an aqueous solution is $(\alpha)_D = +8{\cdot}4°$. The author remarks that the methyladipic ethers differ from the tetra-substituted tartaric ethers by the absence of acid radicles.

Reactions occasioned by the Decomposition of Sodium Thiosulphate in Fixing Photographic Images.—M. Seyewitz and G. Chicandard.—On employing alum and thiosulphate in the proportion of twenty times more thiosulphate than alum, we require, to avoid all decomposition, a weight of commercial sodium bisulphate equal to about the fifth of the weight of the alum. In a mixture of 15 grms. thiosulphate and 60 of alum, we do not require more than the hundredth part of the weight of the alum.

On the Emetics.—E. Maumené.—The author calls in question the formula of tartaric anhydride, or, as he calls it, tetrafilic acid. This formula, he contends, should be written $C8\ {}_{2}H_{2}O8\ {}_{20}$. In a memoir on the hydrocarbides, he has maintained that the ratio $C8=48$ to H_2, or 24 to 1, cannot be true. The exact proportion is 123/5, and not 120 to 5. From an examination of the emetics of silver, sodium, rubidium, potassium (ordinary tartar emetic), and lead, M. Maumené concludes that in an acid, a salt, or any other compound, water can never play a double part (water of combination, water of crystallisation); it is united in a single mass to the anhydrous substance in the general law. An anhydride is that from which we may separate a maximum of water without causing it to lose its essential character. The remark of Berzelius of a constant ratio between the oxygen of the anhydride and that of the bases is not by any means strictly accurate. The composition of all bodies, without exceptions, is subject to the general law of the actions of mixture, sometimes to that of actions of contact, and to no other. The replacements of bodies by others, called substitutions, present always the relations of which we speak, the two terms of which vary exclusively according to the weight of the bodies in action. Isomers, the number of which is greater or smaller in compounds of any nature, vary according to the molecular condensation and the union of the condensed substances with others in the relations of the general law.

New Process for obtaining Dicarbonic Acid (Mellic Acid).—E. Maumené.—The neutral potassium tetrafilate, *i.e.*, tartrate, resists heat up to 280°. At this temperature it becomes coloured if not entirely pure, and loses all the water which it still contains, yielding pure neutral dicarbonate, water, and a little carbon oxide. The salt, very soluble in water, easily yields the acid on transformation into a lead salt and treatment with hydrogen sulphide.

Method of Formation of α-Phenylquinoleine.—Amé Pictet and H. Barbier.—The condensation of formanilide with acetophenone recalls to a certain extent the formation of acridine by the dehydration of formyldiphenylamine, and seems to prove the existence in the pyridic nucleus of quinoleine of a bond between the nitrogen and the carbon γ.

Phenotripyridine.—A. Pictet and H. Barbier.—Phenotripyridine crystallises from alcohol in small prismatic needles, almost colourless. It melts at 236°, and distils unchanged at a much higher temperature. It is insoluble in water, moderately soluble in absolute alcohol and ether, and very soluble in benzene and chloroform. Its character as a tertiary base is shown by the fact that it yields neither an acetylic nor a nitrosic derivative. The authors describe the dehydrochlorate, monohydrochlorate, nitrate, sulphate, and chromate.

Volumetric Determination of Nitric Acid.—D. Monnier and H. Auriol.—By means of an apparatus which cannot be described without the accompanying plate, the authors compare the quantity of hydrogen evolved by causing one and the same quantity of sodium amalgam to react upon pure water, and again upon the aqueous nitric acid in question. The difference of the two volumes corresponds to the hydrogen consumed by the reduction of the nitrates.—*Archiv. Sc. Phys. et Nats. de Genève.*

Adherence of Aluminium and of other Metals to Glass.—Ch. Margot.—Aluminium, magnesium, cadmium, and zinc, to the exclusion of other metals, have the property of leaving upon glass, and in general upon all substances having bases of silica, metallic traces which are not removed by vigorous friction—washing.—*Archiv. Sc. Phys. et Nats. de Genève.*

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on April 1, Sir James Crichton-Browne presiding. The following were elected Members:—Mr. Lockett Agnew, Dr. Julius Althaus, Mr. H. H. Dobree, and Mr. James M. Johnstone. The following will be the Friday Evening Meetings after Easter:—

April 26. John Hopkinson, M.A., D.Sc., F.R.S., "The Effects of Electric currents in Iron on its Magnetisation."

May 3. Veterinary Captain Frederick Smith, "The Structure and Function of the Horse's Foot."

May 10. The Hon. G. N. Curzon, M.P., "A recent Journey in Afghanistan."

May 17. Professor Walter Raleigh, "Robert Louis Stevenson."

May 24. J. Viriamu Jones, M.A., F.R.S., "The Absolute Measurement of Electrical Resistance."

May 31. The Earl of Rosse, K.P., D.C.L., LL.D., F.R.S., "The Radiant Heat from the Moon during the Progress of an Eclipse."

June 7. Professor Alfred Cornu, D.C.L., F.R.S., "Phénomènes Physiques des Hautes Régions de l'Atmosphère."

MEETINGS FOR THE WEEK.

Tuesday, 9th.—Institute of Civil Engineers, 8.
—— Medical and Chirurgical, 8.30.
—— Photographic, 8.
Wednesday, 10th.—Pharmaceutical, 8.30.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1846.

THE SLIT OF A SPECTROSCOPE.

By WILLIAM CROOKES, F.R.S.

One of the most important parts of a spectroscope is the slit, and the best material wherewith to fashion the jaws has been the subject of much thought and experiment in my laboratory for some years past. The substance chosen must be very hard, and capable of being ground to a perfect knife-edge; it must not be granular in texture, or it cannot be worked to the required accuracy; it should not be brittle, or the cleaning which is occasionally necessary will be liable to break the fine edge, and it should be capable of standing any acid vapours to which it is liable to be exposed when left uncovered in a chemical laboratory in active work; it must also not allow light to pass through except between the jaws, absolute opacity at every other part being imperative.

The following extracts from a letter I wrote to my friend Dr. Schumann, in May, 1893, will explain the difficulties, and how they were finally overcome:—

"You may feel interested in knowing the results of some experiments I have been lately making with the object of getting the best material for the jaws of the slit. I again tried iridium, using another piece of well-fused metal; but the old objection of granulation, when the knife-edge stage was reached, was as great as in the former instance. Pure wrought cobalt gives a fine edge, and is very hard and takes a good polish; if nothing better could be got, cobalt would do very well, but I do not know if it would stand the ordinary atmosphere of a laboratory for any long time without tarnishing. Manganese steel is even harder than cobalt, and from what I have seen will make as good an edge: but here the liability of tarnishing is still greater than in the case of cobalt.

"I have recently been making the jaws of my slit of transparent quartz, and I find this answer so perfectly that I cannot conceive anything better. Each jaw of the slit I am now making for the new spectrograph is 25 m.m. long, 13 m.m. wide, and 4 m.m. thick; it is bevelled off along one edge at an angle of 45°, thus:—

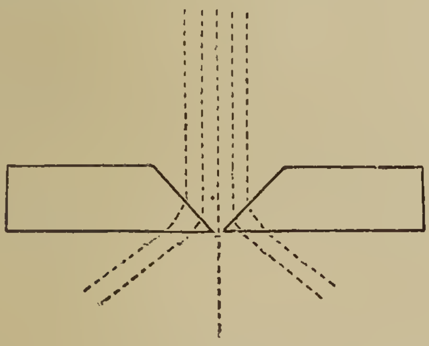

Fig. 1.

"The sides and angle must be ground true and polished. At first I had great difficulty in getting the knife-edge true. In the final grinding and polishing small splinters occasionally broke off the edge, and then I had to recommence the grinding and polishing to get rid of these little flaws. It is difficult for me to fashion a knife-edge of quartz at an angle of 45°. Ultimately I got over this difficulty by putting a very narrow bevel on the front of the plate, so making the angle of each jaw 90° (see fig. 2).

"You at once see that no light can get through the part of the quartz which is cut at an angle, owing to refraction, and the light coming through the flat part of the quartz plate can easily be stopped by a metal diaphragm or film of black varnish. The edge made in this way is absolutely black and opaque even in sunlight, and it will bear a high microscopic power without showing the least irregularity. I clean the slit from dust by opening it about half a millim., and passing a splinter of soft wood between the jaws. I have not yet put a micrometer to the quartz slit, but I see from preliminary experiments that I shall be able to work with a much narrower slit than I could if I used a metal one. It is very beautiful to see the absolute opacity and trueness of edge of one of these slits when examined under a high power."

I have now used nothing else but quartz jaws since the above quoted letter was written, and when properly made I consider them perfect. Besides quartz, several other hard crystals were tried. Sapphire makes good jaws, but being so hard there is corresponding difficulty in getting the edge true; it is also more difficult to get plates of sapphire quite transparent, and in this case perfect transparency is the essential for perfect opacity, for a transparent angle refracts all the light passing through it, and throws it on to the side of the tube, where it is cut off by a diaphragm, whereas a semi-transparent or cloudy crystal disperses some of the incident rays irregularly and makes the background of the image of the slit not absolutely black. In fine spectrum work any stray light illuminating the background is liable to obscure the visibility of faint lines. I tried an edge of a cut diamond, and it answered well, but quartz being hard enough, and so much easier to work, it is not necessary to go to harder crystals.

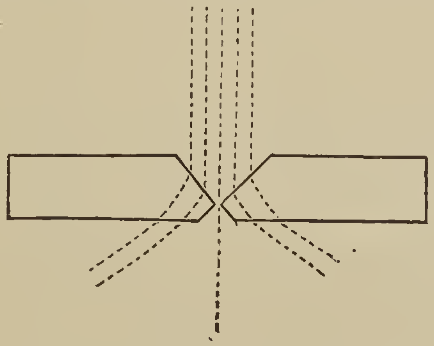

Fig. 2.

If the jaws are cut and polished by a lapidary, the workmen must be warned not to flatten the sharp edge to hide irregularities. I have had several jaws spoiled in that way. The flat face thus formed reflects incident rays, and those of them which are at a sufficiently acute angle to find their way down the tube to the collimator and prisms introduce false light and possibly false lines. The edges of the jaws must be quite straight, so that when they come together they cut off the light at once along the whole length of the slit. This is very difficult to secure, and is one of the reasons why I make the jaws from plates 25 m.m. long. The actual length of working slit not being more than one-quarter of that length it is easy to select sufficient from each jaw to get 5 or 6 m.m. of quite straight edge, even if the whole length is not perfect.

With the pair of jaws in the spectrograph at present in use I can take excellent photographs when they are only 0·0001 inch apart. For eye observations the width can easily be less than that.

Some advantage is gained by making the knife-edges of well-melted quartz. This material is tougher than the crystal and is not so liable to splinter. There is, however, a little difficulty in getting it free from air bubbles.

Formation-heat of Calcium Acetylide.—M. de Forcrand.—The heat sought = +76·95 cal., setting out from solid calcium and gaseous carbon. —*C. R.*, cxx., No. 12.

NEW RESEARCHES BY PROF. RAMSAY ON ARGON AND HELIUM.

M. Berthelot announced, at a recent meeting of the Académie des Sciences, that he had received the following telegram from Prof. Ramsay:—

"Gas obtained by me:—Clèveite; mixture of argon helium. Crookes identifies the spectrum. Make communication to the Academy on Monday."

It appears from this telegram that Prof. Ramsay has made a new and very important discovery, that of a natural mineral containing argon—clèveite. This mineral has been discovered by Nordenskiöld, and consists of uranium oxide and of various rare earths.

In fact, the question concerns an entire group of compounds, known as *uraninites*, in which W. F. Hillebrand has mentioned the presence of an appreciable proportion of nitrogen, capable of being liberated by the influence of acids (*Bulletin of U. S. Geological Survey*, No. 78, 1891, pp. 43 to 79). He has made a special study of this singular reaction, which suggested to Ramsay the idea of a thorough examination. He has thus been led to detect, besides nitrogen, argon and helium.

In fact Ramsay recognises at the same time, in the gases extracted from clèveite, the presence of the spectrum ascribed to a hypothetical element, helium, which has been imagined to account for a special ray of the solar spectrum. Prof. Ramsay has thus discovered a compound of helium.

M. Berthelot, after the Session of the Academy on Monday, received the following letter from Professor Ramsay:—

"I have telegraphed to you to-day announcing the discovery of helium, the unknown element the yellow line of which exists in the solar spectrum.

"Whilst congratulating you on having succeeded in combining argon, I think it will interest you to learn how I have had the good fortune to make this discovery. Hillebrand (of Baltimore) has studied a rare mineral, clèveite. He was surprised to find that this mineral contained about 2 per cent of a gas, the spectrum of which he examined, and found it that of nitrogen. He caused the spark to strike through a mixture of this supposed nitrogen, with hydrogen in presence af sulphuric acid, and obtained ammonium sulphate. It has appeared to me extremely doubtful that any substance could give off free nitrogen after treatment with an acid.

"I took in hand the examination of this gas in the hope of finding a method of combining argon, since Hillebrand has remarked that there existed a definite relation between the nitrogen and the uranium oxide, which, along with lead oxide and rare earths, constitute this mineral.

"On causing the electric spark to strike through a mixture of this gas with oxygen in presence of caustic soda, I obtained a residue (the nitrogen is only present in a minimum quantity). This residue gave the spectrum of argon, and, in addition, another spectrum, the very brilliant yellow line of which does not coincide with the D line of sodium, though approximating to it. The wavelength, measured by my friend Crookes with his magnificent spectrometer, is 587·49.

"There are found, also, other lines less remarkable, in the red, the green, and especially in the violet. All these lines, except the characteristic yellow, have not yet been measured.

"Setting out from the red, and making a comparison with the spectrum of argon, I have found—

Red.—3 identical lines; 2 lines; 1 faint line; 1 line less faint; 1 line strong in He, faint in A.

Orange-red.—1 line equal in both; 1 line equal in both; 1 line equal in both; 2 faint lines.

Orange.—1 faint line; 3 rather strong lines.

Orange-yellow.—2 strong lines; 1 yellow brilliant line in He only (this is the characteristic line of helium); 7 green lines equal in both; 5 greenish-blue lines equal in both.

Green-blue.—1 faint line, not in argon; 1 brilliant line, not in argon.

Blue.—8 rather strong lines, not in argon.

Violet.—3 lines only in A; 2 lines in both, but stronger in A; 4 lines only in He; 2 lines only in both; 1 line only in both; three lines only in both; three lines only in both; 2 lines only in both.

"I have a rather large quantity of clèveite, and one of my assistants has already commenced extracting the gas in a large quantity. My task will be to separate the two substances, which will perhaps not be easy."—*Comptes Rendus*, No. 12, March 25, 1895.

REMARKS ON THE SPECTRA OF ARGON AND OF THE AURORA BOREALIS.

By M. BERTHELOT.

In a matter so novel as the study of argon it may perhaps be useful to suggest some approximating phenomena. From this point of view I take the liberty of mentioning the following:—

It is possible that the rays peculiar to the aurora may be due to a special form or compound of argon, or of elements still unknown, by which it may be accompanied. I request permission to recall a personal observation. During one of my recent experiments upon argon, performed in presence of the vapour of benzene, and with the exceptional circumstances of the rain of fire, there appeared at the ordinary pressnre in the entire extent of the tube a splendid greenish yellow fluorescence, characterised by a spectrum of remarkable rays and bands, and which recalled that of the aurora as far as I could compare them in the hasty conditions of my experiment.

There were perceived independently of the rays of hydrogen and the D rays, various rays—yellow and green, blue and violet—of which I will not fix the position on account of the feeble dispersion of the spectroscope, and the difficulty of comparing fluorescence spectra. I will confine myself to mention a brilliant ray close to the ray D, from which it is separated by a fine black absorption-ray and two groups of bands or broad rays, the one to the left of D in the orange, the other to the right in the yellow and the green, both furrowed by fine absorption-rays. The aspect of these bands was very analogous to that of the group of small rays shown to the left of E in Fig. 1 of Rayet's memoir "On the Spectrum of the Aurora" (*Journal de Physique*, i., p. 366, 1872). I showed these curious phenomena to the young *savants* working in my laboratory. Their analysis deserves to be compared with the spectra of the aurora and of helium.

This observation will thus explain the enigma of the aurora by the production of a fluorescent derivative of argon or of its family contained in the specimen sent me. Angström has already referred to fluorescence in his study on the aurora borealis.—*Comptes Rendus*, cxx., No. 12, March 25, 1895.

Extension to Magnesia of a Method of Synthesis of Fluorides and Silicates.—A. Duboin.—The author has obtained double fluorides of magnesium and potassium. He has found a method which gives well-crystallised products in the case of magnesia and glucina. He melts in a platinum crucible potassium fluoride obtained from the fluorhydrate of potassium fluoride at a bright red heat, and throwing into the melted salt calcined magnesia in small portions. The magnesia dissolves by degrees, as also does glucina. The product has the composition $MgF_2,2KF$. He has also isolated MgO, K_2O, $3SiO_2$.—*Comptes Rendus*, cxx., No. 12.

A DEPHLEGMATOR FOR FRACTIONAL DISTILLATION IN THE LABORATORY.

By SYDNEY YOUNG, D.Sc, F.R.S., and
G. L. THOMAS, B.Sc.,
University College, Bristol.

Various forms of still-head have been devised for use in the laboratory (*vide* "Thorpe's Dict. of Applied Chem.," vol. i., p. 694), those of Wurtz, Linnemann, Le Bel, and Henninger and Glinsky being most frequently used.

Another form of dephlegmator, resembling in construction that employed in the Coffey still, has been recommended by F. D. Brown (*Trans. Chem. Soc.*, 1880, 49), but has not met with the attention it seems to deserve.

FIG I

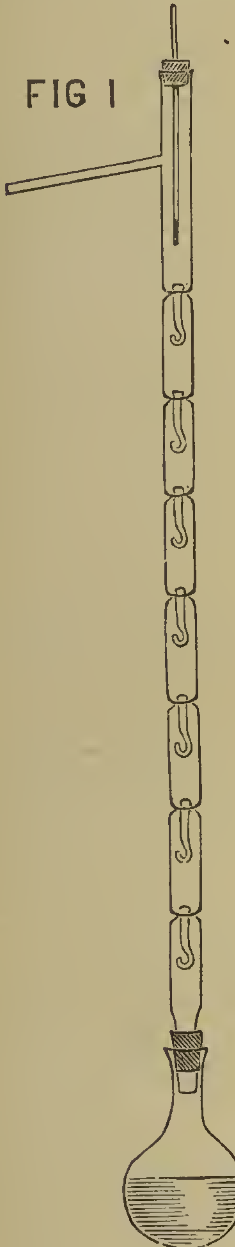

FIG 2

We have for some little time made use of a dephlegmator (Fig. 1) similar in principle, but differing from Brown's in construction; and as it has been found convenient, and has given very good results, we think that a description of it may be useful.

A glass tube, about 18 m.m. in internal diameter, is sharply constricted at intervals of about 8 c.m. (The constrictions may be formed by heating the tube, kept in regular and rather rapid rotation, with a small blowpipe flame, then producing a partial vacuum in the tube by drawing in with the breath). On the constricted portions of the tube rest discs of platinum-gauze, through the centre of which pass glass tubes of the form and dimensions shown in Fig. 2. The vapour passes through the condensed liquid resting on the platinum discs, and the excess of liquid flows down the tubes, resting on the discs.

While the distillation is proceeding, the pressure of the vapour forces the liquid up into the wider part of the dropping-tubes; if the tubes are too narrow above the head of liquid, there is danger of bubbles of vapour being caught and carried down, so as to empty the tubes, when the ascending vapour might find an easier passage through the tubes than the gauze. With the tubes constructed as shown in the diagram, this has never been found to occur.

As soon as the distillation is stopped, the level of the liquid falls to that at the lower end of the dropping-tubes, and this small quantity of liquid is easily recovered by removing the dephlegmator from the flask, and sending a small, but sharp, blast of air through the side tube.

In order to test the efficiency of the dephlegmator a mixture of 200 grms. of pure benzene and 200 grms. of pure toluene was distilled—(1) from an ordinary distillation-bulb with a still-head 30 c.m. long (from the bulb to the side tube); (2) from a flask with a plain still-head, 110 c.m. in length; (3) from a flask with a dephlegmator of the same length with seven constrictions.

The results are given in the table below;—

Temperature corr. to 760 m.m.	Weight of fraction in grms.		
	Short still-head.	Long still-head.	Dephlegmator.
80·2 to 83·2	0	0	36·5
83·2 ,, 86·3	0	1·2	99·6
86·3 ,, 89·4	9·0	48·4	22·3
89·4 ,, 92·5	99·4	94·4	20·3
92·5 ,, 95·6	86·9	51·8	18·8
95·6 ,, 98·7	54·8	36·3	19·5
98·7 ,, 101·8	35·8	30·6	15·1
101·8 ,, 104·8	30·0	26·4	5·3
104·8 ,, 107·9	30·9	22·0	18·9
107·9 ,, 110·3	53·0	51·9	36·5
110·3 ,, 110·9			40·1
Pure toluene 110·9°		36·2	66·1
	399·8	399·2	399·0

It will be seen that the separation with the long still-head is considerably better than with the short one, but that neither of the plain still-heads can compare at all in efficiency with the dephlegmator.

After three additional fractionations with the dephlegmator, 175 grms. of pure toluene and 60·8 grms. of pure benzene were recovered; two further fractionations of the partially purified benzene brought up the weight of the pure substance to 174·4 grms. The weight of each pure substance recovered amounted, therefore, to over 87 per cent.

We are at present using a dephlegmator 125 c.m. long with twelve constrictions, the flask being supported by a retort-stand and clamp on the floor and the condenser on the working table.

ON THE

PROPERTIES OF AMORPHOUS SILICON.

By M. VIGOUROUX.

In a former paper we have indicated that it is possible, under certain conditions, to reduce silica by magnesium, and to obtain an amorphous silicon quite free from foreign bodies. The properties of this substance are as follows:—

Physical Properties.

It is a fine powder, of a maroon colour, and adheres to any moist or rough surface. It readily absorbs gases and watery vapour, and requires for their expulsion to be heated to near redness; its mean specific gravity at 15°

is 2·35°. It may be melted and easily volatilised in the electric furnace. It is soluble in a great number of metals in a state of fusion.

Chemical Properties.

It does not seem to be affected by heat. It has been practicable to raise it for a long time to high temperatures without any alteration in its properties, which depends on the strong heat liberated at the moment of its preparation. Hydrogen has no action. Fluorine attacks it at common temperatures.

In chlorine silicon ignites at 450°, and in bromine about 500°; in iodine there is neither incandescence nor apparent reaction.

In the oxygen of the air there is superficial oxidation without incandescence. In pure oxygen there is brisk combustion about 400°, and the heat is such that the silicon formed is melted.

In sulphur incandescence occurs about 600°. In nitrogen it does not react below 1000°; at a higher temperature it attacks. In silicon it forms an amorphous nitride. Phosphorus, arsenic, and antimony, if heated with it, distil without reactions. Carbon and boron act only in the electrical furnace. The metals seem not to combine with silicon at temperatures generally available in laboratories. Magnesium alone yields a silicide with lively incandescence.

Dry gaseous hydracids attack it slowly about dull redness. Hydrogen sulphide, if gradually heated up to its dissociation-point, does not act upon the silicon. Ammonia is decomposed at cherry-redness; hydrogen is liberated and the nitrogen combines with the silicon, forming a nitride.

Watery vapour is decomposed at the same temperature, forming silica and hydrogen, which escape. The decomposition is continuous, but slow. Sulphurous anhydride, if passed over silicon at about 1000°, is not reduced. Nitrous and nitric acid act slowly towards 800°, with fixation of nitrogen and oxygen. If the reaction is lively there is incandescence. Phosphoric anhydride is reduced with incandescence before a red-heat. It is the same with the oxygenc ompounds of arsenic and antimony. Between 800° and 1000° carbonic anhydride is reduced to the state of carbon monoxide. The latter is not attacked even at 1200°. Silicon is not attacked by any acid dissolved, or liquid, if acting alone, nor by fuming nitric acid heated to ebullition, nor by sulphuric acid concentrated and boiling, nor by concentrated hydrofluoric acid if heated with it to 100°. The combined action of two acids, or of an acid and another body, is often effective. Thus aqua regia at 100° acts in course of time, and ultimately transforms it into anhydrous silica. A mixture of nitric acid and hydrofluoric acid attacks it at the common temperature with an escape of muddy fumes and of silicon fluoride. Hydrofluoric acid, mixed with potassium nitrate or chlorate, acts with violence; it is the same with ordinary nitric acid if mixed with potassium fluoride.

Silver fluoride is decomposed with incandescence before a red-heat; there are formed silicon fluoride and silver, which is set at liberty, and is found in small melted grains. It is the same with zinc and lead fluorides, &c.

Most oxides are reduced in glass tubes heated with a Bunsen burner, in many cases with incandescence; such are mercury, copper, lead, bismuth, tin, iron, manganese oxides, &c. The alkaline and alkaline earthy oxides are attacked energetically.

Hydrofluoride of potassium fluoride seizes the silicon and liberates hydrogen. Lead sulphate and calcium phosphate are reduced. The silicon may be thrown upon potassium chlorate in decomposition without incandescence, but this phenomenon occurs if the two substances are intimately mixed and then heated. Potassium nitrate reacts only at its decomposition temperature. The alkaline carbonates, whether in solution or fusion, convert it into silica. Certain oxidising agents, such as potassium dichromate and lead chromate, are decomposed with incandescence and explosion below a red-heat. The mixture of fuming nitric acid and potassium chlorate has no appreciable action.

The amorphous silicon obtained by reducing silica with magnesium corresponds neither to the amorphous varieties α or β of Berzelius. It approximates rather to crystalline silicon. Nevertheless the latter has hitherto been regarded as incombustible in oxygen. This indifference is only apparent. If we raise the temperature abruptly, the crystalline silicon ignites at 400° in oxygen, and burns with a dazzling lustre. If it is finely powdered the combustion may be complete.—*Comptes Rendus*, cxx., p. 367.

THE CHEMOMETER.*

By W. OSTWALD.

(Concluded from p. 168).

In like manner, it may be shown that the differences of the chemical and electrical potential must increase or decrease in the same direction. For this purpose we only need suppose the existing differences of chemical and electrical intensity, compensated by a suitable number of circuits introduced, and to apply the above conclusions.

We may, therefore, accept the result as certain, that, in fact, the electrometer may serve as a chemometer. The question now arises as to the extent in which this process is applicable. Since it is connected with the fact the chemical process is proportional to the electrical, the presence of electrolytes is a necessary condition of the method. As to what minimum of electric conductivity we can go depends on the question, With how little electricity the electrometer can act? It is now a peculiarly favourable circumstance that the quantities of electricity adhering to the ions are extremely large, so that quantities of matter far beyond the limits of the ponderable can yield quantities of electricity very sufficient to set the electrometer in action. We may, in fact, in this direction complain rather of too great than of too small sensitiveness. On the other hand, it is certain that the sphere of electrolytes extends very much beyond the aqueous solutions of acids, bases, and salts. A relatively great number of organic compounds may be, without doubt, appended to the ordinary electrolytes. It is here also a question of continued experimental elaboration to extend the process gradually further and further. Even that which is already accessible will require for its experimental elaboration the work of a number of years.

Finally, I must advance another question. Electric energy is only one of those which accompany chemical changes; but as we always see changes of volume, or in solutions variations of osmotic pressure, connected with chemical reactions, we must conclude that also the energy of volume may furnish aids to the measurement of chemical potential or of affinity. Indeed, if we reflect that the modern theory of chemical circuits refers their action everywhere to the activity of osmotic pressures, *i.e.*, to the changes of volume energy, we find in the latter the fundamental inseparable from the chemical process, whilst for obtaining chemical energy as electrical we always require peculiar arrangements.

In fact, for a great number of chemical reactions we may carry out perfectly similar considerations in which pressure plays a part similar to that of electromotive force. We know also that for solutions and gases the magnitude of capacity is proportional to the energy of volume and the volume is proportional to the magnitude of chemical capacity, and for quantities comparable (the molecular weights) is equal in magnitude. There appear, also, relations quite similar to the foregoing, though with a difference very essential for the experimental phase of the

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* From the *Zeitschrift fur Physikalische Chemie.*

question. The free, or changeable, electricity is simply equal to the product of the quantity of the electricity into the difference of potential, and the latter is the measure of the same, as the former, according to Faraday's law, is alike for quantities of different substance which are chemically equivalent. The volume energy, on the contrary, appears in the only case hitherto accessible, that of volumes and gases, as the product of the volume into the difference of the logarithms of the two pressures. For equal differences of the chemical potential the pressures increase, not in an arithmetical, but in a geometrical, series, and soon arrive in a region inaccessible to measurement.

To take an instance. If a difference of the chemical potential expressed electrometically by 1 volt, correspond in the most favourable case to the relation of two pressures, the one 10^{17} times greater than the other. If we take as the smallest measurable pressure $\frac{1}{1000}$ of an atmosphere, the other would amount to 10^{14}, *i.e.*, 100,000 millions of atmospheres, whilst our means of measurement scarcely exceed 1000 atmospheres. As, moreover, chemical potentials have been measured up to three or four volts in electrical measure, we arrive at the quite inconceivable values of 10^{48} or 10^{65} atmospheres, which we require, in the most favourable case, to ascertain what the electrometer tells us without any difficulty.

SYNTHETIC EXPERIMENTS IN THE PYRAZOL SERIES.*

Part I.

By R. von ROTHENBURG.

(Concluded from p. 165).

Hydrazin seems to form a pyrazolidon with cinnamic acid, as the oily product here also takes a transitory blue-green product with nitrous acid.

On Pyrazololidon.

This compound cannot be obtained by the action of equal mols. of hydrazin hydrate and malonic ester. On the contrary, malonic ester and hydrazin form the readily soluble malonhydrazidic acid, which on heating forms pyrazololidon with abscission of water and the closure of the ring.

It is obtained as follows:—Equal mols. hydrazin hydrate and malonisteric acid are mixed, after dilution, with 3 vols. alcohol to prevent a too violent reaction. The mixture is then boiled for half an hour and distilled from the oil-bath. At 195—205° there passes over a yellow oil of an intense odour. The sparingly soluble dimalonylhydrazin was not present in the mixture even before distillation.

Ferric chloride colours the new substance violet-blue; it dissolves in alkali with a yellow colour; as also readily in water, especially hot, and in the usual solvents. Strong mineral acids and alkali split off hydrazin on brisk ebullition.

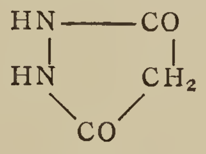
(4)-Benzal-pyrazololidon.—With benzalaldehyd there is formed a reddish yellow condensation-product, the properties or which offered no guarantee of purity.

(4) - Isonitroso - pyrazololidon is formed on passing nitrous acid into the aqueous solution of pyrazololidon, and dissolves very readily with a lemon-yellow colour. On mixture with ammonia and silver nitrate, and subsequent careful neutralisation with acetic acid, there is deposited the lemon-yellow compound, (4)-Isonitroso-pyrazololidon silver.

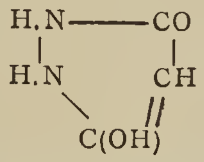
Pyrazololidon-(4)-*p*-azotoluol is obtained by the ordinary method for preparing the azo-derivatives of the pyrazolons, taking especial care for good refrigeration. The bright reddish yellow colouring-matter is precipitated by acids. This strongly acid substance is much yellower than the corresponding compound of pyrazolon. It is decidedly more soluble in organic solvents, and crystallises from glacial acetic acid in small, shining, yellow-red crystals, fusible above 250°.

Constitution of the Pyrazololidons. Isomerism and Tautomerism of the Pyrazololidons. Course of Reaction, and Conditions of their Formation.

The pyrazololidons have the general formula—

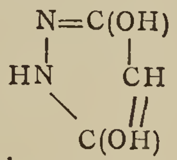


with the tautomerous by-form analogous to the pyrazolons:—



with which the behaviour with diazo-salts and the circumstance that the metallic salts contain only 1 equiv. of metal agree perfectly.

Whether there exists also a second pseudoform—



must remain doubtful.

The pyrazolidons arise from derivatives of bibasic acids in which both carboxyls are linked to a single carbon atom. A condition of this formation is that both the carboxyl-groups possess a differently intense capacity of reaction with hydrazin, as there are otherwise formed symmetrical di-substitution products.

A COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF PYRITE AND MARCASITE.*

By AMOS PEASLEE BROWN.

(Concluded from p. 172).

The important point brought out in these experiments is that pyrite contains a large amount of ferric iron, while in marcasite the iron apparently exists in the ferrous condition. Some reducing action might, however, have taken place, due to the sulphides formed. The condition of the iron in the chlorides found in the boat and tube was very carefully tested by several reagents in each case, and there can be no doubt as to the correctness of the results as stated above.

The decomposition of the sulphides by metallic salts seemed to offer some hope of being productive of results that would show in a quantitative way the exact amounts of ferrous or ferric iron that are present in these two minerals. In this line, the action of gold chloride, silver nitrate, and silver sulphate were tried in a qualitative way with both minerals. Of these the first gave a ready decomposition with both, and produced both ferrous and ferric salts in each case. The silver nitrate gave a similar result. Silver sulphate acted very slowly and without any definite results.

The action of copper sulphate in neutral solution and under pressure was tried with very remarkable results.

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* From the *Journal Praktische Chemie.*

* Read before the American Philosophical Society, May 18, 1894 —From the *Proceedings of the American Philosophical Society,* xxxiii., No. 145.

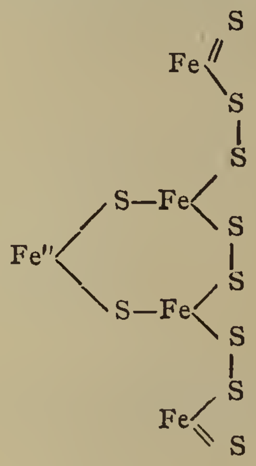
At the ordinary temperature and pressure the solution of this salt has little effect on either mineral, and the same is true of the solution at a boiling temperature, but under pressure the reaction is complete. The experiment was conducted as follows:—0·2 grm. of the finely pulverised mineral was introduced into a stout glass tube, and 50 c.c. of a 10 per cent solution of the salt, $CuSO_4.5H_2O$, added, the air displaced with a pinch of $NaCO_3$, and a drop or two of H_2SO_4 (dilute), and a heavy seal made on the tube. The tubes containing the two minerals were heated for six hours in an autoclave to a temperature of about 200°. The contents of the tubes were found to contain no traces of undecomposed mineral, but there was a black, more or less flocculent precipitate in its place. This proved to be copper sulphide. The solution had not altered appreciably in appearance. The liquid contents of the tube were in each case transferred to a flask previously filled with CO_2 and with 10 c.c. dilute sulphuric acid in the bottom, the tube then rinsed with water and the amount of ferrous iron present titrated with freshly standardised potassium permanganate. In the case of marcasite this gave 18 c.c. $KMnO_4$ solution (this was two- or three-tenths of a cubic centimetre too much, on account of the difficulty in catching the end-reaction). To correct this for the iron in the copper sulphate, a blank of 50 c.c. $CuSO_4$ solution, the same as used above with 10 c.c. dilute sulphuric acid, was titrated with the permanganate, giving 0·5 c.c. reduction. The factor of the permanganate was 0·0054 grm. Fe for 1 c.c. Making the correction for the reduction of 50 c.c. $CuSO_4$ solution, this gives 47·25 per cent of iron in solution as against 46·67, the theoretical amount in FeS_2. No doubt if the end reaction had been more exact there would have been a still closer correspondence in the result.

The tube containing the pyrite was treated in exactly the same manner, and gave a reduction of permanganate of 3·8 c.c. This time the end reaction was sharp and exact. Calculating the above to iron (after making correction for $CuSO_4$) this gives 8·91 per cent of ferrous iron in pyrite. As the total iron is 46 67, this corresponds to 19·09 per cent of the iron in the mineral, or almost exactly one-fifth. These experiments demonstrate in a positive manner the condition of the iron in the two minerals, and even show the exact amounts of each condition of the iron, ferrous and ferric.*

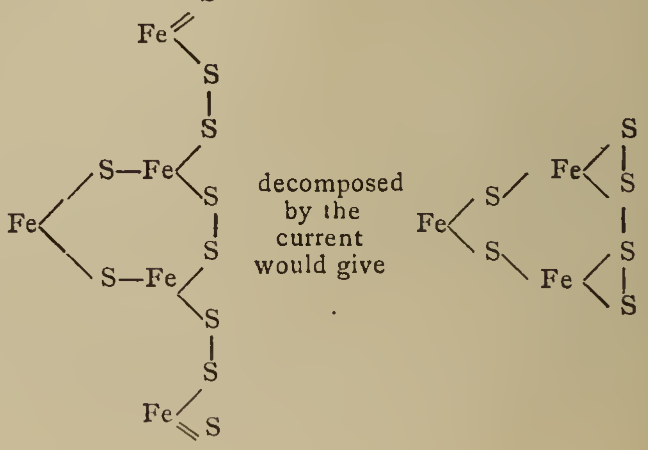
That marcasite should hence be be more readily decomposed by oxidation than pyrite seems fully explained by the foregoing investigations, as it consists of $Fe''S_2$, an unsaturated compound. In this compound sulphur must link to sulphur, or the compound have unsaturated bonds, and hence any element which would attack the sulphur would break up the compound. On the other hand, the iron is held to the sulphur by its full number of bonds, and any substance that has an affinity for iron could not so readily attack it in this condition, This would be true whether ferrous iron be considered here as Fe_2, with a valence of four, or as Fe''. That marcasite is $Fe''S_2$ is also indicated by its oxidation in the air into $FeSO_4$ mainly. Under these same conditions it will be noted that pyrite forms both ferrous and ferric compounds, as $FeSO_4$, but much more $Fe_4O_3(OH)_6$ and free sulphur. Marcasite, however, when decomposed by water under pressure (in nature) forms much limonite also, this being due no doubt to the oxidation being effected under pressure. This constitution explains also the fact that the oxidation of marcasite is continuous and complete, as shown by the current oxidations. It will be shown also that this constitution of pyrite that has been made out explains fully its action with the current. That marcasite is unsaturated is also indicated by the fact that it has not been made artificially or at any rate positively identified in any of the artificial FeS_2 that has thus far been made. If marcasite be a persulphide, as its formula would seem to indicate for a ferrous compound, none of the methods detailed above for making FeS_2 would be applicable in its case, unless perhaps the method of Deville might produce it. All of the other methods would probably produce ferric iron, at least in large part, and the resulting product would be pyrite.

The formula for pyrite derived from my investigations and expressing the relation of the two conditions of the iron in the simplest way is $4Fe^{iv}S_2{\cdot}Fe''S_2$. This formula is also borne out by what we know of the formation of pyrite as given in the early part of this paper, and by such experiments as I have made on its decomposition, as well as the fact above alluded to, that it, in oxidising in nature, does not form much ferrous compounds, but mainly ferric. And it also explains the fact that it is more stable as regards any element attacking its sulphur, for it is most probable that all the sulphur of the $Fe''S_2$ in its formula is linked to iron. I would propose the following structural formula, not as expressing the exact constitution of the compound, for of that we know nothing, but as an expression of the condition of the iron in the molecule and as embodying in a quantitative way the result of my investigations into its constitution. It will be noticed that the sulphur of the $Fe''S_2$ is made to link entirely with iron.

Structural formula of pyrite.



If ferric iron be considered as Fe^{iv}—Fe^{iv} it is only necessary to connect the ferric Fe atoms with bonds, but it seems to me that ferric iron is more likely Fe''', and at any rate this is the simplest way to regard it. A very striking proof of the correctness of the idea expressed in this structural formula that $Fe''S_2$ in pyrite has its sulphur all linked to iron is afforded in the experiments on oxidation of the mineral by means of the electric current as detailed above. It will be recalled that the amount thus oxidised was between 21 and 22 per cent. Now if two molecules of FeS_2 be split off from the above formula, say those linked by sulphur to sulphur, there would remain a saturated compound much more difficult to decompose (theoretically) than the pyrite molecule illustrated, and the amount of sulphur thus removed would be by calculation 21·33 per cent. This action could be thus illustrated.



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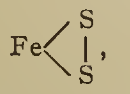
* These results have been confirmed by experiments made during the past year in this laboratory, and not yet published.

Of course this structural formula is only intended to represent the probable relations of the atoms in the molecule, and the probability that the $Fe''S_2$ is entirely saturated.

A structural formula for marcasite might be given as—



and this really expresses our entire knowledge of its constitution. It may be any polymer of this, for being unsaturated it should be capable of forming polymers.

I much regret that want of time has compelled me to discontinue these latter investigations into the decomposability of these minerals by solutions of metallic salts under pressure, as it seems to open up a way for the study of many other sulphides, and would doubtless be productive of most valuable results. Besides this, it would probably adduce additional proof of the correctness of my formulæ for these minerals as given above.

Acknowledgment.

I take this occasion to express my sense of gratitude to Prof Edgar F. Smith, who suggested the work to me, and who, by his constant encouragement and ready advice, has greatly furthered its prosecution. Many of the experiments were made at his suggestion, and no doubt the success of the work is largely due to him.

NORTH CAROLINA MONAZITE.*

By H. B. C. NITZE.

Monazite is a phosphate of the rare earths cerium, lanthanum, and didymium. It also contains thoria and silica, which are present in varying percentages. The mineral is subtranslucent, light yellow, or yellowish brown or green, and has a resinous lustre. Its hardness is from 5 to 5·5, and its specific gravity 4·9 to 5·3. Its economic value lies principally in thoria, which it contains; this is used as one of the constituents in the manufacture of mantles for the Welsbach and other incandescent gas lights.

The mineral is somewhat widely distributed, but has been found in commercial quantities only in Brazil, Siberia, Norway, and North and South Carolina in this country. The North Carolina area embraces between 1600 and 2000 square miles, situated in Burke, McDowell, Rutherford, and Cleveland counties. The principal deposits of this region are found along the waters of Silver, South Muddy, and North Muddy creeks, and Henry and Jacob's Forks of the Catawba river in McDowell and Burke counties; and the Second Broad river in McDowell and Rutherford counties; and the First Broad river in Rutherford and Cleveland counties. Some monazite is also found in Polk county, and along the western edge of Catawba, Lincoln, and Gaston counties.

The best crystallised specimens have been found at Milholland's Mill and Stoney Point in Alexander county. The monazite occurs in the sands and gravels of the stream-beds, associated with other minerals, such as quartz, felspar, hornblende, epidote, mica, magnetite, garnet, zircon, rutile, corundum, &c. The primary source of monazite is in the crystalline gneisses and schists, of which it is an accessory constituent. The material produced from the disintegration of the decomposed country rock is deposited in the stream-beds, and undergoes, by virtue of a continual current and differences of specific gravity, a natural process of partial sorting and concentration. The richer portions of the stream deposits are thus, as a rule, found near the head-waters.

As the percentage of thoria is variable in different sands, the value of the mineral consequently varies accordingly, and must be determined by careful chemical analysis. Some monazite contains practically no thoria. It is stated that the transparent greenish and yellowish brown varieties are usually the richest. The best north Carolina sands (highest in thoria) occur near Brindletown, Burke county, and in the northern part of Cleveland county. Some of the highest grade Brindletown sand runs from 4·00 to 6·60 per cent of thoria; sand from Gum Branch in McDowell county is reported to run 3·30 per cent thoria; some sand from near Shelley in Cleveland county contains 2·76 per cent thoria.

The thickness of these stream-gravel deposits is from 1 to 2 feet, and the width of the mountain streams in which they occur is seldom over 12 feet. The sluice-boxes used in separating it are about 8 feet long by 20 inches wide by 20 inches deep. Two men usually work at a box, the one digging the gravel and shovelling it into the box, the other one working it up and down in the box with a gravel-fork or perforated shovel in order to float off the lighter-sands.

These boxes are cleaned out at the end of the day's work, the cleaned monazite being collected and dried. If it contains magnetite it is treated with a magnet. It is then ready for packing and shipment. From 20 to 35 lbs. of cleaned monazite sand, per hand, is considered a good day's work. The value of the best grades of sand is 6 to 7 c. per pound at the diggings.

During the past two years the following shipments of monazite sand have been made from this region :—

In 1893: 110,000 lbs. at 6 c. at mines, 6600 dols.; 20,000 lbs. at 5 c. at mines, 1000 dols.; total, 130,000 lbs., 7600 dols. In 1894: 460,000 lbs. at $6\frac{3}{4}$ c. at mines, 31,050 dols.; 80,000 lbs. at 6 c. at mines, 4800 dols.; 6855 lbs. at 5 c. at mines, 342.75 dols.; total, 546,855 lbs., 36,192.75 dols.

THE CAUSE OF LUMINOSITY IN THE FLAMES OF HYDROCARBON GASES.*

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.

In a paper read before the Chemical Society in 1893, I showed that in the inner non-luminous zone of a flame of ordinary illuminating gas, the hydrocarbons originally present in the gas, and consisting of ethylene, butylene, benzene, methane, and ethane, became converted by the baking action of the walls of flame between which they had to pass into acetylene, and that, at the moment when luminosity commenced, over 80 per cent of the total unsaturated hydrocarbons present consisted of this compound.

The presence of acetylene at the point where luminosity commenced naturally suggested that it was in some way due to actions in which the acetylene played the principal part—either that it split up into carbon and hydrogen under the influence of heat, and so supplied the flame with the solid particles necessary, according to Sir Humphry Davy's theory of the cause of luminosity, or else by its polymerisation it formed the dense vapours required by Dr. E. Frankland's more recent hypothesis.

In order to elucidate this point, I carried out the long series of experiments upon the action of heat upon flowing ethylene and other hydrocarbons, which formed the subject of communications to the Royal Society in 1893 and early this year, in which I showed that whilst flowing through a heated area (the temperature of which was between 800° and 1000° C.), ethylene decomposed according to the equation—

$$3C_2H_4 = 2C_2H_2 + 2CH_4.$$

and that the acetylene then polymerised into a large

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* Read at the Sixty-Eighth Meeting of the American Institute of Mining Engineers, Florida.—From the *Engineering and Mining Journal*.

* A Paper read before the Royal Society.

number of more complex hydrocarbons, amongst which benzene and naphthalene were conspicuous, whilst at temperatures above 1200° C. no polymerisation took place, but the acetylene formed from the ethylene decomposed at once into carbon and hydrogen, whilst the methane, which up to this temperature had been but little affected, decomposed into—

$$2CH_4 = C_2H_2 + H_2,$$

and this fresh supply of acetylene at once broke up to carbon and hydrogen, so that at temperatures above 1200° C. the complete action might be looked upon as being—

$$C_2H_4 = C_2 + 2H_2.$$

These results have an important bearing upon the cause of the luminosity in the flame, as it is manifest that if the temperature of the luminous zone is above 1200° C., the light emitted must be due to incandescent particles of carbon, and not to incandescent hydrocarbon vapours.

On determining the temperature of an ethylene flame whilst burning from a small fish-tail burner by means of the Le Chatelier thermo-couple, used in the way described in my paper (*Chem. Soc. Journ.*, 1893) on the luminosity of coal-gas flames, I found that the temperatures were as follows:—

Portion of Flame.	Height above Burner.	Temperature.
Non-luminous zone	½ inch	952° C.
Commencement of luminosity	1¼ „	1340
Top of luminous zone ..	2 „	1865
Sides of „ „ ..		1875

Showing that luminosity commenced at 1340° C., and continued even at 1875° C., temperatures at which the incandescent vapour theory becomes untenable.

It might be urged that the heavy hydrocarbons already produced at a lower temperature in the non-luminous zone are not so easily decomposed by heat as acetylene, and that these may be causing the luminosity, even though carbon particles be present from the decomposed acetylene; but this would hardly be possible, as so little besides acetylene is to be found at the top of the non-luminous zone of an ethylene flame, and it can be experimentally shown that, even when benzene vapour is formed and is largely diluted, it begins to break up and deposit carbon at 1200° C.

The supporters of the "solid particle" theory of luminosity agree in concluding that the liberated carbon, existing as it does in a condition of molecular division, is heated to incandescence partly by its own combustion, and partly by the combustion of the hydrogen and carbon monoxide going on around the finely-divided carbon particles.

As has been pointed out by many observers, it is clear that the carbon particles themselves undergo combustion, otherwise they would escape unburnt from the flame, whilst it is manifest that the combustion of hydrogen and carbon monoxide, which plays so important a part in the flame, must add its iota to the temperature attained by them.

Both these sources of temperature, however, would be manifest in the flame itself, and with flames of given size burning from the same description of jet we ought to find that their luminosity is governed by—

A. The temperature of the flame.
B. The number of carbon particles in a given area.

Moreover, we should expect that the higher the temperature of the flame, the whiter would be the light emitted, so that a comparatively low temperature flame, even when rich in carbon particles, would be yellow and lurid as compared with a flame containing the same or a smaller number of particles, but which had a higher temperature.

It has been pointed out by Prof. A. Smithells (*Phil. Mag.*, 1894, p. 249) that it is erroneous to consider the temperature of a flame as being the temperature recorded by thermometric instruments inserted into the flame, as by such devices you only obtain the mean temperature of a considerable area of the flame uncorrected for loss from conduction.

It is also perfectly well known that in a flame a thick platinum wire may only be heated to redness, whilst a thin wire may even be fused; and this suggests that flame temperatures taken by the Le Chatelier thermo-couple of platinum and platinum-rhodium wires may be totally incorrect. In using this beautiful and convenient device, I have found that the length of the wires twisted together made practically no difference in the recorded temperature, and that one twist was as good as six.

In all my flame experiments I have made the twist as short as possible, and, by always using wires of the same thickness, have obtained results which are at any rate comparable if not correct; and in order to find what difference the thickness of the wires would make, I got Messrs. Johnson and Matthey to draw for me wires of 0·018, 0·011, and 0·003 of an inch diameter, and having calibrated the galvanometer scale for temperature with thermo-couples of the same length of twist made from each of them, obtained the following results with the same portion of a Bunsen flame.

Wire used.	Temperature shown.
0·018	1617° C.
0·011	1728
0·003	1865

These results show that the diameter of the wire seriously affects the temperature recorded under these conditions by the thermo-couple, the same degree of heat being recorded by the fine wire as being 248° hotter than is shown by the thickest wire employed, this discrepancy being probably chiefly due to loss by conduction,

In taking the temperature of heated gas flowing through a tube this source of error is but small, as, some considerable length of wire being heated on each side of the twist, conduction has but little effect on the thermo-couple itself; but in determining the temperature of flames it is manifest that the finest usable wire must be employed in order to reduce the error from conduction. Test experiments also showed that no part of the thermo-couple must project beyond the flame, as if it did a considerable diminution in the recorded temperature took place.

For these reasons it was manifestly best to use the finest wire which could be employed without the risk of fusing at the temperatures existing in the flames to be tested; and all temperatures recorded in this paper were made with wire 0·011 inch in diameter, the twist being as short as possible, so that it is probable that, although the temperatures may be from 100° to 200° too low, yet the results are strictly comparable.

Experiments which I have lately made with pure acetylene, prepared by the action of water upon calcic carbide, shows it to be the most powerful illuminant to be found amongst the gaseous hydrocarbons, as when burnt in a small flat flame burner under the most suitable pressure, and its illuminating power calculated to a flow of 5 cubic feet an hour, its value is equal to about 240 candles.

The colour of the flame is pure white, and an ethylene flame beside it looks yellow and dull—the purity of the light at once suggesting a very high condition of incandescence in the particles of carbon present in the flame.

On now taking the temperature of the various portions of the flame, and comparing these with the temperatures obtained in the same way with the ethylene flame and a coal-gas flame of the same size, the following results are obtained:—

Portion of Flame.	Acetylene.	Ethylene.	Coal Gas.
Non-luminous zone ..	459° C.	952° C.	1023° C.
Commencement of luminosity	1411	1340	1658
Near top of luminous zone	1517	1865	2116

whilst the illuminating value of the gases calculated to a flow of 5 cubic feet an hour in the burners best suited for their consumption are—

Acetylene	240·0
Ethylene	68·5
Coal gas	16·8

whilst if all were compared when burning from flat-flame burners of the same size as those in which the temperatures were determined, the results, when calculated to a consumption of 5 cubic feet an hour, would be—

Acetylene	211·0
Ethylene	31·5
Coal gas	nil.

Here, then, we have the anomaly of three gases, which not only do not conform to the preconceived expectation, but which have their ratio of temperature and illuminating value directly opposed to each other.

In the case of the acetylene and ethylene, moreover, the molecules contain the same number of atoms of carbon, and yet we obtain so enormous a discrepancy in their illuminating value.

The fact that there is no apparent relation existing between the temperature of the flame, or the probable number of carbon particles contained in it and its illuminating value, at once suggests that the luminosity must be in great part governed by some thermo-chemical changes taking place in the flame itself, and which do not of necessity affect the average temperature of the flame to any great degree.

The researches of Hittorf (*Wied. Ann.*, vii., pp. 587, 591) and Siemens show that air, steam, and the oxides of carbon, even when heated to temperatures above those existing in luminous hydrocarbon flames, are perfectly non-luminous; and the fact that the Bunsen flame, when supplied with sufficient air, has a temperature exceeding 1800° C. in its hottest part, and yet emits no light, shows us that it is exceedingly unlikely that any interactions leading to luminosity take place amongst these ordinary flame gases.

The fact that most of the unsaturated hydrocarbons in the flame are converted into acetylene before luminosity commences, naturally draws one's attention to this body, and the fact that it is highly endothermic at once suggests the idea that it may be the liberation of heat during its decomposition that endows the carbon particles produced from it with an incandescence far higher than any which could be expected from the temperature of the flame.

Berthelot has calculated that the temperature developed by the detonation of acetylene at constant volume is no less than 6220° C., and if this be imparted at the moment of its liberation to the products of its decomposition, the incandescence of the carbon particles is at once explained.

If luminosity be even partly due to this cause, the detonation of pure acetylene first recorded by Berthelot should develope light, and, in order to see if this were so, a thin glass tube, closed by a cork, had a detonator containing one-tenth of a grm. of mercuric fulminate suspended in it by two copper wires, which were connected by a thin platinum wire in contact with the fulminate, and on firing the detonator by the electric current the flash of the fulminate was found to emit but a feeble light.

The same charge was fixed in a similar tube filled with pure acetylene collected over mercury, the result being a flash of intense white light and the shattering of the tube, the pieces of which were thickly coated with the carbon produced by the decomposition of the acetylene.

Moreover, the small piece of white tissue paper used to contain the fulminate was only scorched at the points where the explosion of the fulminate had burst through it, showing that in the instantaneous decomposition which had taken place the intense heat which had been developed either was confined to the products of decomposition, or else had hot had time to scorch the paper.

The experiment at first sight seemed conclusive evidence that it was the endothermic nature of the acetylene which, during its decomposition in the flame, endowed the particles of carbon with the necessary incandescence, but the objection presented itself that, when exploding mixtures of oxygen and hydrogen in the eudiometer, a distinctly luminous flash is produced, and, although the light so obtained is feeble as compared with the intensity of the white light produced by the detonation of the acetylene, still further proof is necessary before this action can be accepted as the prime factor in producing luminosity.

It is also manifest that it would not do to assume that the rapidity of the decomposition of the acetylene in a flame was nearly so great as when the undiluted gas was detonated, and the question arose as to whether it would be possible to obtain evidence as to acetylene, when exposed to heat alone, liberating carbon in a luminous condition.

Although the instantaneous liberation of heat on the decomposition of the gas by detonation appears to confine the temperature to the products of its decomposition, it was to be expected that, on being decomposed by heat, and probably, therefore, at a slower rate, the increase in temperature might be detected.

To try this, pure acetylene was passed through a platinum tube, 2 m.m. in diameter and 40 c.m. long, in which the Le Chatelier thermo-couple was arranged as follows:—The two wires were twisted together for a length of 3 m.m., and the wires on either side of the twist are then passed through thin glass tubes, which are fused on to them; having been in this way coated with glass so that only the twist is exposed, they are passed through the platinum tube, the glass insulating the wire from the metal of the tube, and also keeping the thermo-junction in such a position that it registers the temperatures of the gas in the tube, not that of the wall of the tube. To each end of the platinum tube glass T-pieces are fitted, down the stems of which the wires pass to mercury seals; from the metal seals conducting wires lead to the resistance-coils, the key, and a reflecting galvanometer.

A steady flow of acetylene was allowed to pass through the tube, and was led into water at the other end. The tube was slowly and carefully heated for about 4 inches of its length, and, as the temperature reached 700° C., white vapours began to flow from the tube, and these, as the temperature rose, increased in quantity. The source of heat had been so regulated that the temperature had risen about 10° per minute, but, almost immediately 800° C. was passed, the galvanometer registered a sudden leap up in temperature to about 1000° C., whilst finely-divided carbon poured from the tube. This seemed to indicate that 800° was about the temperature at which the pure acetylene broke up into its constituents, and an experiment was now made to see if this developed incandescence in the liberated carbon.

(To be continued).

NOTICES OF BOOKS.

Chemical Analysis of Oils, Fats, Waxes, and of the Commercial Products derived therefrom. From the German of Professor Dr. R. Benedikt. Revised and Enlarged by Dr. J. Lewkowitsch, F.I.C., F.C.S. 8vo., pp. 683. London and New York: Macmillan and Co. 1895.

We generally look with distrust upon foreign scientific books rendered into English by a foreigner, since, though fully understanding the original, he is in general not sufficiently acquainted with the resources of our tongue. The instance before us forms a signal exception. We find in it nothing which might not have come from the pen of an educated Englishman.

Dr. Lewkowitsch refers to the wearisome prolixity of

Continental chemists in describing analytical processes. This fault is as largely indulged in by American writers.

Passing to the subject-matter, we must pronounce the work before us of exceeding value. Not only are the oils and fats very sparingly endowed with those striking properties which serve us in the diagnosis of metals, but they and their preparations have been seized upon by the greed of the present age, and falsified with a perseverance worthy of a better cause. Hence though their properties, physical and chemical, have been diligently scrutinised, cases still arise where the judicious analyst is not enabled to pronounce a decided opinion as to the presence or absence of fraudulent admixtures and substitutes,—"surrogates," as our German neighbours call them. Further, not a few oils and fats vary in their properties, according to the country where they have been produced, the conditions to which they have been subject, and the age of the sample.

Amongst the physical methods here described spectroscopical examination takes a place. An admixture of vegetable oils with those of animal origin may be detected by the absorption bands due to the presence of chlorophyll. "Olive and linseed oils give three absorption bands,—a very dark one in the red, a faint one in the orange, and a distinct one in the green." According to Daumer, the oils may be arranged spectroscopically in four classes:—

"1. Oils showing the spectrum of chlorophyll: olive oil, hemp-seed oil, and nut oil.

"2. Oils without any light-absorbing power: castor and almond oils.

"3. Oils absorbing the (so-called) chemical rays of the spectrum — the red, orange, yellow, and part of the green, remaining unabsorbed.

On examining such oils the spectrum from red to green remains quite normal, while the other parts are invisible. Here belong rape oil, linseed oil, and mustard-seed oil.

"4. Oils showing absorption bands in the different parts of the spectrum: sesame oil, arachis oil, poppy-seed oil, and cotton oils."

Concerning the value of the refractive power of different oils, authorities are not quite unanimous. The refractometers of Abbe and Zeiss are here figured and described, as also the oleo-refractometer of Amagat and Jean, based on an arbitrary scale.

The polariscope yields also results of some value, the instrument used being Laurent's saccharimeter, having a tube of 20 c.m. The microscopical appearance, the electric conductivity, and the determination of the specific gravity are also employed. The instrument preferred for this last determination is Stohmann's picnometer. Recourse has also been had to the melting- and solidifying-points.

But in all these tests, as well as in the chemical reactions, much trouble and frequent discrepancies arise from the great difficulty of obtaining for comparison samples of absolute purity. We suspect that analysts have sometimes been knowingly and intentionally supplied with sophisticated or abnormal specimens, in order to lead them and their colleagues into errors and bring the scientific examination of oils into mistrust and contempt. The pattern test first proposed by Tomlinson, and subsequently developed by Wynter Blyth, gave definite results only after a very prolonged series of experiments.

The chemical methods most used in the analysis of oils are the saponification value, the Reichert-Meissl value, the iodine and bromine values, and the acetyl value. The Maumené test—the rise of temperature observed on adding concentrated sulphuric acid—is rightly considered a valuable method for detecting sophistications, especially in the case of olive oil—the kind most liable to fraudulent admixtures,

Colour reactions, it is here pointed out, must be used with extreme caution, since small quantities of foreign substances, purposely or accidentally present, may give misleading indications.

The question of rancidity is ably treated. It is shown (Ballantyne and Heyerdahl) that free fatty acids alone do not occasion rancidity. Nor is this change due to the action of micro-organisms. Ritsert has shown that bacteria, whether aërobic or anaërobic, speedily die if introduced into fat. Rancidity seems due to the joint action of air and light. The larger the proportion of stearic and palmitic acids in a fat, the less is its liability to rancidity. The generally rancid condition of palm oil is doubtless due to the dirty manner in which it is collected by the natives.

We cannot prolong our notice of this interesting work. It will prove of the utmost value to all persons using oils and fats in the arts,—and they are a very numerous body,—as well as to analysts. Dr. Lewkowitsch has greatly enriched our technical literature by reproducing Prof. Benedikt's work in an English dress.

Organic Chemistry: the Fatty Compounds. By R. Lloyd Whiteley, F.I.C., F.C.S., Principal of Municipal Science School, West Bromwich. Crown 8vo., pp. 291. London and New York: Longmans, Green, and Co. 1895.

The author of this work confines himself to the so-called fatty compounds, which have lately enjoyed a smaller share of attention than the aromatic series.

After some useful introductory matter, touching chiefly on the sources and the purification of organic substance, he goes on to ultimate analysis of organic compounds, to the determination of percentage composition, and of molecular formulæ. Here we find an exposition of the determination of vapour density and of Raoult's cryoscopic method. Both these operations are necessary in research, and both are less generally known to chemists than would be desirable.

In speaking of the constitution of carbon compounds, Mr. Whiteley does not forget to caution his readers that the bonds have no actual existence, and are merely a convenient method of expression.

In the successive sections of the work the author discusses the fatty hydrocarbons, the haloid paraffins, the monohydric alcohols and their derivatives. The unfortunate fact is here mentioned—though without comment—that in Britain the official and commercial alcoholometric standard is not absolute, but "proof spirit." This is, we think, quite as unscientific as the retention of our traditional weights and measures.

In Section III. we have an account of cyanogen and its derivatives, substances which latterly, since the introduction of the coal-tar colours, have lost much of their technical importance.

In successive sections there follow the derivatives of the unsaturated hydrocarbons, of the dihydric and the polyhydric alcohols. It may edify certain orators to find that the name alcohol is no longer the exclusive property of the liquid against which they are contending, but a generic term.

The instructions given in this work, though necessarily concise, are clear and accurate, and the illustrations are exceedingly well drawn. There are here no lists of questions which have been set at examinations, nor references to any "syllabus," or any other of the characteristic features of the cram-system. Students who wish to *know* will find Mr. Whiteley's work a trustworthy guide.

Annual Report on the Year 1894. By E. Merck, Darmstadt. Published in March, 1895.

The very appearance of this work in the English language is a proof of the remarkable enterprise of its publisher. The Report consists of three parts. Of these, the first is composed of original communications; the second is devoted to pharmaceutical preparations; and the third to drugs.

Of these sections the second displays an admirable amount of research, which cannot fail to be of great value in medical practice, and to bear ultimate fruit in the treatment of disease.

The nomenclature is to some extent that recognised among German physicians and pharmacists; but certain features liable to puzzle an English reader, and leading him to mistake, *e.g.*, chloride for chlorate, have been avoided.

The weights and measures used are chiefly those recognised in England, and when the metric system is followed it is specially pointed out.

This pamphlet is, on the whole, written in very correct English. We may, however, point out that with us the symbol for iodine is I, not J.

List of Apparatus, &c., required for Teaching Practical Elementary and Advanced Physics, in accordance with the New Science and Art Regulations. Manufactured and Sold by Philip Harris and Co. (Ltd.) Edmund Street, Birmingham.

The list comprises elementary apparatus for a two years' course of experimental study. There are also sets of apparatus for the more advanced student in heat, sound, light, magnetism, and electricity. We are happy to notice that the optical apparatus includes a table spectroscope, the use of which instrument has been hitherto too much neglected in this country. The same must be admitted concerning the polariscope and saccharometer. We are bound to mention that the prices for the apparatus are exceedingly reasonable. No one can complain of having to pay, *e.g.*, £6 10s. for a table spectroscope properly fitted, or £3 10s. for a usable microscope.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 12, March 25, 1895.

New Researches by Prof. Ramsay on Argon and Helium.—M. Berthelot.—(See p. 176).

Remarks on the Spectra of Argon and of the Aurora Borealis.—M. Berthelot.—(See p. 176).

Researches on the Metals of Cerite.—P. Schützenberger.—This memoir will be inserted in full.

New Method of the Preparation of Chloroplatinous Acid and its Salts.—Leon Pigeon.—The author takes the reducing agent in weight equal to the theoretic quantity which should react. The chloroplatinic acid which is to be transformed is first weighed. The crystals which it produces when the solution is evaporated answer to the formula $PtCl_6H_2+6H_2O$. A mol. of this product (517 grms.) is exactly saturated by 1 mol. of barium carbonate, pure and dry (197 grms.), which is weighed out before allowing it to react. The liquid then contains exclusively barium chloroplatinate. He then weighs out a mol. of barium dithionate, crystalline, $S_2O_6Ba+2H_2O=333$ grms. This substance is dissolved in three times its weight of hot water. The two liquids are then mixed in a flask closed completely with a glass stopper. The flask is heated to 100° in the water-bath for twenty-four hours, when it is gradually modified, and takes the red colour of the chloroplatinites.

Action of Ortho-amino-benzoïc Acid upon Benzoquinone.—J. Ville and Ch. Astre.—Ortho-amino-benzoïc acid behaves with benzoquinone like the primary amines with simple functions. The formation of the product obtained from the acetic mother-liquors shows that benzoquinone presents certain properties common to the diacetones.

Variations of Saccharine Matters during the Germination of Barley.—P. Petit.—Saccharose increases continuously, but slowly, from the third to the sixth day. Diastase makes its appearance only on the fourth day.

Chemical Process for the Purification of Waters.—F. Boardas and Ch. Girard.—The authors use calcium permanganate, which removes organic matter and all micro-organisms. The reactions are:—Decomposition of the calcium permanganate in presence of organic matter with formation of calcium carbonate and manganese oxides; oxidation in the mass (composed of coke and manganese oxide) of the lower oxides of manganese at the expense of the excess of calcium peroxide; lastly, slow reduction of the manganese peroxide thus formed by the organic matters, or by the coke itself.

Formation of a Perfect Vacuum, even in Large Recipient, without any Mechanism.—M. de Laurier.—The receiver is filled with a gas, such as oxygen, capable of being absorbed by iron heated to redness.

Revue Universelle des Mines et de la Metallurgie. Vol. xxviii., No. 3.

Process for Enriching Phosphatic Limes.—P. Tarbary.—Hitherto the enrichment of calcareous phosphates has been aimed at by the removal of worthless matter. The calcium carbonate has been causticised by burning, and has then been dissolved away in water. The author proposes to use the phosphatic limes or basic slags in the iron manufacture, in place of common limestone.

Discovery of a Deposit of Calcium Phosphate in the Cretaceous Deposits of Brabant.—Prof. G. Lambert.—This deposit has been found in sinking an artesian well at Brussels. The proportion of phosphate has been found to be from 9 to 11 per cent, at depths of 108 to 122 metres.

Annual Production of Phosphates in the World.—

	Tons.
Belgium	450,000
France	450,000
England (coprolites)	20,000
Germany (coprolites and phosphorites)	50,000
Spain	50,000
Russia	75,000
Norway (apatites)	20,000
Algeria	7,000
Canada	20,000
North Carolina	7,500
South Carolina	600,000
Florida	500,000
Mexico (guano)	5,000
South America (guano)	60,000
Haiti	2,000
India	20,000

Consumption of Chemical Manures.—

	Tons.
Austria	100,000
Belgium	300,000
France	1,100,000
Germany	1,500,000
Holland	150,000
Italy	100,000
Norway and Sweden	100,000
Britain	1,100,000
Spain	100,000
United States	1,555,000

—*Le Phosphate.*

MISCELLANEOUS.

Electro-Chemistry in France.—The Société Industrielle of Rouen is offering a Gold Medal, among a number of others, for a new application of electro-dynamic machines to the chemical industry. All competitive essays, drawings, &c., are to reach the President of the Society by the 2nd September next.

The late Prof. von Helmholtz.—It is proposed to erect a statue in memory of the late Prof. von Helmholtz, and a Central Committee has just been formed in Berlin in connection with the matter. A Sub-Committee has also been appointed to convene meetings in various towns in connection with the movement, and also to organise in large local committees. Already a large number of subscriptions have been received.

Bismuth Nitrosalicylates.—H. Causse.—It results that even in a dilute solution nitric acid combined with bismuth oxide transforms salicylic acid into β-nitrosalicylic acid capable of yielding a series of salts the aspect of which varies with their composition. This property of nitrosalicylic acid seems to be due to the group NO_2 in its molecule. As in the other nitro-compounds, the phenolic function is heightened. Its aptitude for combination being thus rendered greater, explains the existence of a series of compounds previously obtained with salicylic acid. The presence of iron is not indispensable for the red colouration of bismuth salicylate.—*Bull. de la Soc. Chimique de Paris.*

MEETINGS FOR THE WEEK.

Wednesday, 17th.—Meteorological, 8.
—— Microscopical, 8.
Friday, 19th.—Quekett Club, 8.

THE CHEMICAL NEWS.
Vol. LXXI., No. 1847.

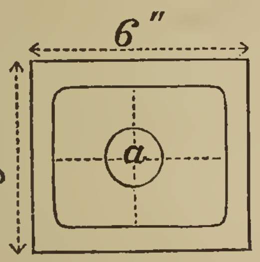
ON THE DIMINISHING OF PIPING IN CRUCIBLE-STEEL INGOTS CAST FOR TOOL MANUFACTURE.

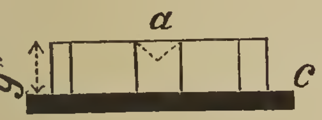
By SERGIUS KERN, M.E, St. Petersburg.

We think the following short notice will be of interest to metallurgists.

In order to avoid as much as possible the nuisance of piping in ingots, we propose the following method for casting crucible-steel used in the manufacture of various workshop tools, made by forging:—

The cast iron moulds into which the charge of each crucible (⅜ of a cwt.) is poured into, are of the following design:—





The stand, *b*, is a block of cast-iron 3 inches thick; the lid is 2 inches thick (not shown). The mould is open from both ends, and is 2 inches thick. The dotted lines show the direction of the cutting of the steel ingots, previously heated, under the steam-hammer; the centre, *a*, is cut out, and is refuse (the pipe). The four blocks obtained are heated and drawn out into suitable bars.

SOLUBILITY AS A CLUE TO THE GENESIS OF THE ELEMENTS.

By C. T. BLANSHARD, M.A.

For the subject of solubility, in so far as it bears on the genesis of the chemical elements, the authorities that I have consulted are:—1. "Watts' Dict. Chem.," last ed.; 2. Storer, "First Outlines of a Dictionary of Solubilities," Cambridge, U.S., 1864; 3. R. Godeffroy, B.* 9, 1363 (coefficients of solubility of salts of the alkali metals).

Of the theories of solubility, so far propounded, *e.g.*, Berthelot and Jungfleisch (Bl. 13, 303), who regard solution as intermediate between simple mixture and chemical union; S. U. Pickering (B. 24, 3629), who explain solution as due to residual chemical affinity, the investigations of A. Belohoubek, of Prague (quoted shortly in C.C. 1880, p. 446); and of T. Carnelley (P.M. [5], 13, 180), are those which throw most light on the genesis of the elements. Belohoubek proves that of organic substances consisting of carbon and hydrogen, with or without oxygen—1. Substances free from oxygen are insoluble in water; 2. The richer a compound in oxygen, the more soluble it is in water; 3. Bodies dissolve each other better the more closely they resemble each other in structure.

Carnelley showed that of two or more isomeric bodies, that one dissolves most easily which has the lowest melting-point and in which the atomic arrangement is the least symmetrical.

Accurate data as to solubility at present to hand are the following, in which the solubility is reduced to uniform terms for the sake of comparison, namely the ratio of the weight of substance to the weight of water (that being the solvent considered as affording most data) required to dissolve it at a constant temperature, 15°.

Salt.	Solubility.	Salt.	Solubility.
LiCl	1 in 1·4 of water.	LiBr	1 in 0·6 of water.
NaCl	1 in 3·0 ,,	NaBr	1 in 1·3 ,,
KCl	1 in 2·8 ,,	KBr	1 in 1·5 ,,
RbCl	1 in 1·25 ,,	RbBr	1 in 1·0 ,,
CsCl	Very soluble.	CsBr	?
$LiNO_3$	1 in 1·5 of water.	Li_2SO_4	1 in 3 of water.
$NaNO_3$	1 in 1·4 ,,	$Na2SO_4$	1 in 7 ,,
KNO_3	1 in 5·0 ,,	K_2SO_4	1 in 10 ,,
$RbNO_3$	1 in 0·5 ,,	Rb_2SO_4	1 in 2·5 ,,
$CsNO_3$	1 in 8·0 ,,	Cs_2SO_4	1 in 0·5 ,,

With the exception of $CsNO_3$, the same regularity is observable as in the other groups of salts.

In the Zn group we have reliable data only in the case of the chlorides.

Salt.	Solubility.	Salt.	Solubility.
$ZnCl_2$	1 in 1·2 of water.	$ZnSO_4$	1 in 2 of water.
$CdCl_2$	1 in 3 ,,	$CdSO_4$	1 in 5? ,,
$HgCl_2$	1 in 14 ,,	$HgSO_4$	Decomposed by water.

Much more complete data are available for the alkali earths.

Salt.	Solubility.	Salt.	Solubility.
$BeCl_2$	Very sol. in water.	$Be(NO_3)_2$	1 in 0·5 of water
$MgCl_2$	,, ,, ,,	$Mg(NO_3)_2$	1 in 1·0 ,,
$CaCl_2$	1 in 0·25 of water.	$Ca(NO_3)_2$	1 in 3? ,,
$SrCl_2$	1 in 1·5? ,,	$Sr(NO_3)_2$	1 in 5 ,,
$BaCl2$	1 in 2·0 ,,	$Ba(NO_3)_2$	1 in 12 ,,
$BeSO_4$	1 in 1 ,,		
$MgSO_4$	1 in 3 ,,		
$CaSO_4$	1 in 360 ,,		
$SrSO_4$	1 in 7000 ,,		
$BaSO_4$	1 in ∞ ,,		

Only sporadic examples of solubility are to be had in the Si and P groups; therefore I shall not quote compounds of these. In the iron groups we have the following results:—

Salt.	Solubility.	Salt.	Solubility.
$FeCl_2$	1 in 2 of water.	$CoCl_2$	Slowly sol. in water.
$RuCl_2$	Insol. in ,,	$RhCl_2$	Insol. in water.
$OsCl2$	Sol. in small quantity of water, decomposed by large.	$IrCl_2$	,, ,,
$NiCl_2$	Very sol. in water.		
$PdCl_2$	Slightly sol. in ,,		
$PtCl_2$	Insol. in water.		

Chlorides of the halogens and chlorides and sulphates of the Al group furnish fairly comparable data.

Compound.	Solubility.	Compound.	Solubility.
BCl_3	Decom. by water.		
$AlCl_3$	1 in 1·4 of water.	$Al_2(SO_4)_3$	?
$ScCl_3$	?	$Sc_2(SO_4)_3$	?
YCl_3	Sol. in water.	$Y_2(SO_4)_3$	1 in 30 of water.
$LaCl_3$	Very sol. in water.	$La_2(SO_4)_3$	1 in 5 ,,
FCl	?		
ClCl	Rather sol. in water.		
BrCl	Sol. in water.		
ICl	Very sol. in water.		

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* Abbreviations as in "Watts' Dictionary."

We derive from the above figures, though in some cases they are rather meagre, together with Belohoubek's generalisations, the following laws of solubility :—

1. Bodies dissolve each other the more they resemble each other in structure.
2. In salts of groups II. and II.A. (*metallic* groups; for this division of the elements see P.M. [5], 39, 108) the solubility in water varies inversely as the atomic weight of the metal.
3. In salts of group I. (metallic elements) the solubility in water gradually decreases to the third member, potassium, and then increases until it reaches a second maximum with cæsium.
4. In salts of the intermediate and non-metallic groups (though here data are very defective), the solubility in water varies directly as the atomic weight of the metal, or electro-positive element.

Thus, according to law (1), simple compounds are soluble in water, more complex compounds in more complex liquids, as ether, alcohol, benzene, &c. This law, applied originally by its author to organic substances, admits of extension to all bodies, whether elements or compounds. Thus, many metals are soluble in hydrogen, as palladium. A still larger number are soluble in carbon, as Fe, Mn, Ni, Al. Metals also dissolve in each other, sometimes to an indefinite extent, but very generally to form alloys of definite constitution, able to crystallise. This is exactly analogous to salts crystallising with definite amounts of water.

Again, non-metals, which are, as a rule, insoluble in water, dissolve in various organic substances, as benzene, carbon disulphide, &c. Metals which dissolve in each other and in hydrogen, or the element carbon, are insoluble in such complex bodies.

It follows, therefore, that non-metals, from the point of view of solubility, are more complex, and therefore more highly evolved substances than metals. Sulphates, which are not of such simple structure as chlorides or bromides, or even as nitrates or chlorates, having more atoms in the molecule, are, as a rule, less soluble.

A good example of higher evolution, as indicated by increasing complexity of the solvent with increase of atomic weight of the non-metallic constituent, is to be found in the halogen salts of silver :—

AgF, soluble in water.
AgCl, very soluble in ammonia.
AgBr, soluble in ammonia.
AgI, nearly insoluble in ammonia.

Or, taking the actual figures for the solubility in ammonia only, we have, according to "Watts' Dictionary," reduced to a uniform standard as before—

AgF, very soluble in ammonia.
AgCl, 1 in 14 of ,,
AgBr, 1 in 20 of ,,
AgI, 1 in 2500 of ,,

New Volumetric Process for the Determination of Nickel.—F. Lecœuvre.—The process depends on the immediate precipitation of nickel by potassium cyanide in a solution feebly ammoniacal, and on its re-solution in an excess of the reagent. The solution of cyanide is at 10 per cent; each c.c. corresponds to 22 or 23 m.grms. of nickel. It is standardised with a solution of nickel and ammonia double sulphate. The commercial salt contains about 14·93 per cent of nickel. The author operates at the common temperature, adding to the neutralised solution a few c.c. of ammonia at 5 per cent. He runs in the cyanide by degrees, stirring constantly, until an additional drop transforms the turbid liquid into a transparent yellowish solution. The liquid must not be diluted. The presence of ammoniacal salts or of a small quantity of ammonia does not interfere.—*Revue Universelle des Mines et de la Metallurgie*, xxviii., No. 3.

RESEARCHES ON THE METALS OF CERITE.

By P. SCHÜTZENBERGER.

NOTWITHSTANDING numerous determinations the atomic weights of the metals of cerite do not seem to be established with all the certainty which might be desired. There is here no question of a precision of the order of that introduced by Stas in the determination of equivalents. The differences between the numbers proposed by various experimentalists bear most frequently upon the whole numbers, and sometimes reach several units.

Thus for cerium, the one whose oxide is easiest to separate in a high state of purity, the value of the atomic weight has varied from 137·1 to 142·3; the most recent determinations of Brauner (1885) and of Robinson (1884) approach closely to 140 (139·75 to 140·43).

It is evident that discrepancies so considerable cannot be ascribed to the degree of precision used in the analyses, but depend on causes of errors inherent in the methods employed. I have sought, by means of a series of experiments conducted methodically, to account for the nature of these disturbing causes, so as to avoid them. My attention has been specially directed to the analysis of cerium sulphate, a salt easy to obtain in a state of great purity, and in the form of fine crystals, by evaporating its aqueous solutions on the water-bath, taking advantage of its less solubility in hot than in cold water.

The excellent method due to an eminent and regretted colleague, Debray (fusion of the nitrates with eight or ten times their weight of saltpetre, between 320° and 330°), enables us easily and quickly to separate cerium in the state of dioxide from the didymium and lanthanum oxides, the nitrates of which are much more stable and only begin to decompose above 400°. If the operation is repeated two or three times, it yields a cerium oxide quite free from didymium and lanthanum. I indicate rapidly how I have obtained the pure cerium sulphate which has served for my experiments, following known methods except in some details :—

1. Treatment of the pulverised cerite with concentrated sulphuric acid.

2. Solution of the sulphates in pure water after expelling the excess of sulphuric acid; filtration; precipitation by hydrogen sulphide.

3. Evaporation of the liquid on a boiling water-bath in a capsule, an operation in which there separates rose-coloured crystalline crusts, formed of a mixture of cerium, didymium, and lanthanum sulphates.

4. The crystals separated from a ferruginous mother-liquor are dehydrated, re-dissolved in cold water, and the solution evaporated anew on the water-bath gave a purer deposit, which was re-dissolved; the solution is precipitated by ammonium oxalate. The mixture of oxalates, washed and dried, is dissolved in heat in an excess of pure nitric acid, and heated to the complete destruction of the oxalic acid. The solution of the nitrates is evaporated to dryness, the residue is mixed with 8 parts of saltpetre; the mixture is melted, and kept in fusion between 310° and 325° until the cessation of all escape of nitrous vapours.

5. The yellow cerium dioxide which separates is isolated by washing with hot water; the washing is completed with a solution of ammonium nitrate, to prevent the cerium dioxide from passing through the filters in a milky state. After ignition it is re-converted into sulphate, into oxalate, and lastly into nitrate, which is submitted to a second fusion with saltpetre at 320°. We thus eliminate the didymium which has been carried down on the first fusion, and we obtain a dioxide the solution of which no longer presents the absorption rays of the salts of didymium,

6. The white dioxide, faintly yellowish, thus obtained is transformed into cerium sulphate by concentrated sul-

phuric acid; the cerium sulphate is heated a little below an incipient dull red, and converted into cerous sulphate, $2[(SO_4)_2Ce] = (SO_4)_3Ce_2 + SO_3 + O$.

This last is dissolved in cold water, and the clear filtrate is evaporated on a boiling water-bath. The cerous sulphate is gradually separated during the evaporation in colourless prismatic crystals. When a large quantity has accumulated against the sides of the capsule, the mother-liquor is decanted off; the dehydrated crystals are redissolved in the cold, and the solution is separated in the water-bath, which furnishes a second crystallisation and a second mother-liquor.' This new crystallisation is heated like the first. We continue thus, repeating the same series of operations five or six times. Finally, the last crystallisation may be regarded as sufficiently pure, and may serve for the analyses.

The crystals are crushed and dried in a boat through which is passed a current of dry air, whilst it is heated to 440° by means of the vapour of sulphur. All the water of crystallisation is thus expelled without separating the least trace of sulphuric acid. Under these conditions the salt loses 13·66 per cent of its weight, which corresponds to 5 mols. of water for an atomic weight of cerium bordering on 139·5. Without entering into the details of the numerous experiments effected in order to seek out the causes of errors inherent in the various methods which may be followed in the analysis of pure cerium sulphate, I will confine myself to indicating the conclusions at which I have arrived.

It is not possible to determine the sulphuric acid exactly by precipitating with barium chloride a boiling solution of cerium sulphate acidified with hydrochloric acid. However we may proceed—as has been already observed by Marignac—the barium sulphate carries down with it cerium oxide in the form of sulphate or chloride, or in both states simultaneously. In fact this barium sulphate, after being well washed and ignited, becomes yellow if it is moistened with concentrated sulphuric acid and ignited again. The weight of cerium thus carried down, if calculated as sulphate, may reach 2·2 per cent of the crude barium sulphate. The weight of the barium sulphate obtained, augmented by that of the cerium sulphate carried down, coresponds to a higher weight of barium sulphate not formed.

The carrying down of the cerous salt may be avoided by proceeding as follows:—

The solution of cerous sulphate is poured into an excess of a hot solution of pure caustic soda, obtained by dissolving sodium in water. The whole is kept for some time in ebullition. The precipitate of cerous oxide is washed with boiling water by decantation. The filtrates are collected, acidulated with hydrochloric acid, and precipitated in heat with a very slight excess of barium chloride. If formed under these conditions the barium sulphate subsides well, and never passes through the filters as it does if we use a decided excess of barium chloride.

If thus applied this method yields results which do not present between one experiment and another a satisfactory agreement, or the atomic weights thence deduced are generally too high, and vary between 140 and 141·5. The error is due to the circumstance that a small fraction of the sulphuric acid is retained by the precipitate of cerous oxide in spite of the intervention of an excess of hot caustic soda.

We succeed in overcoming this difficulty by dissolving the cerous hydrate, washed by decantation in hydrochloric acid, and re-precipitating in pure soda. During these washings the cerous hydrate absorbs a little oxygen, and is partly converted into ceric hydrate insoluble in dilute hydrochloric acid; but this fact, which is little marked, does not interfere with the success of the operation. The analysis, if thus conducted, gives 123·30 barium sulphate for 100·00 anhydrous cerous sulphate, which leads to the atomic weight 139·45 for cerium, a value probably not far remote from the truth.

Brauner's method (ignition of anhydrous cerium sulphate, and weighing the residual dioxide) seems to avoid every cause of error by reason of its great simplicity. The results furnished are nevertheless variable, and depend on the temperature at which the ignition of the sulphate is effected. At a cherry-redness we expel the totality of the sulphuric acid; the weight of the residual oxide (CeO_2) leads to an atomic weight included between 139·8 and 140. If, on the contrary, we heat for some time to a white redness, the oxide loses weight, and the atomic weight calculated is 139·8 to 138·8. This variation may be explained by admitting a slight loss of oxygen, which is the more probable as we have to do with a peroxide.

We arrive at analogous conclusions if we proceed by synthesis:—A known weight of cerium dioxide is converted into cerium sulphate by means of concentrated sulphuric acid. The cerium sulphate, if moderately ignited near—yet below—incipient dull redness, is converted into white anhydrous cerous sulphate. After weighing with exclusion of moisture, the salt is dissolved in water, and collected again to weigh it and take account in the calculation of the small quantity of dioxide not attacked.

With the dioxide very light and finely divided, of a light lemon-yellow colour, obtained by burning cerous oxide at a low temperature, the results lead to the atomic weight 143; the same oxide heated for some time to dull redness gives 140·5 to 141; lastly, after prolonged ignition to a bright redness, almost white, we obtain again the value Ce = 139·0, which is given by the ignition of the sulphate at this temperature.

Hence the methods founded on the transformation of the sulphate into dioxide, or inversely on the conversion of the dioxide, want a fixed basis. In both cases the numbers vary with the temperature, and we have the right to ask to what temperature of ignition does the true cerium dioxide correspond?

The following experiment proves that oxides richer in oxygen than the dioxide may be formed by mere oxidation in the air, and without the assistance of oxygenated water:—

Cerous oxide precipitated by pure soda, well washed with boiling water, collected on a filter, and then dried on the stove at 100°, dries up in the form of a yellow porous mass; this mass, if dried at 440° and then at dull redness, loses between the two temperatures 0·7 per cent of its weight, and a further 0·7 per cent between dull redness and a cherry-red. It is on account of these uncertainties concerning the true composition of the peroxide in question that we are led to give the preference to the atomic weight 139·5, deduced from the analysis of cerous sulphate in the moist way.

In the course of these researches we have observed the following facts:—

The cerium dioxide obtained by two or three successive fusions with saltpetre at 320°, being converted into cerous sulphate quite free from didymium and lanthanum, if we fractionate in successive portions the crystals during evaporation of the solution on the water-bath, we find a decrease of the atomic weight of cerium calculated from the weight of the residue of the ignition (at bright redness) of the sulphate, a residue calculated as dioxide.

The following series, taken among many others which have given similar results, shows it distinctly:—

Crystallisation	No. 1	Ce = 139·4
,,	No. 2	Ce = 139·05
,,	No. 3	Ce = 138·06
,,	No. 4	Ce = 135·2.

This decrease shows plainly the presence of strange earths in the cerium dioxide obtained by Debray's method. We shall soon return to this interesting point.—*Comptes Rendus*, cxx., p. 668.

THE CAUSE OF LUMINOSITY IN THE FLAMES OF HYDROCARBON GASES.*

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.

(Continued from p. 183).

A SMALL glass combustion tube was well supported, and heated to the highest temperature attainable with one of Fletcher's big blowpipes, whilst pure acetylene was slowly flowing through it, the heating not being commenced until the tube was filled with the pure gas, all air being thoroughly rinsed out. As the temperature reached the softening point of the glass, the acetylene apparently burst into a lurid flame at the point where it entered the zone of heat, and clouds of carbon swept forward through the tube; but, although the carbon particles had to traverse an inch or more of tube more highly heated than the point of entering the hot zone, it was only at this latter point that the luminosity was developed, proving beyond doubt that it was the heat evolved by the decomposition, and not the external heating, which caused the carbon particles to emit light.

If it is the decomposition of the molecule of acetylene which develops the heat which is the cause of the incandescence of the carbon particles, then, if acetylene could be burnt without decomposition, a non luminous flame should be produced. It is conceivable that this might be done by so diluting the acetylene that it would require a much higher temperature to break it up.

It was Heumann who showed (*Liebig's Annalen*, clxxxiii., Part I., pp 102—131) that hydrocarbon gases may burn with luminous flames, *i.e.*, with separation of carbon in the flame, or with non-luminous flames, *i.e.*, without any separation of carbon, and that the maintenance of a high temperature is an essential condition of luminosity; a flame, the temperature of which has been lowered by any means, being no longer able to bring about the required separation of carbon. He also points out (*Ibid.*) that "combustible matter, when diluted with indifferent gases, requires to be maintained at a higher temperature, in order that it may burn with a luminous flame, than when it is undiluted with such gases."

Dr. Percy Frankland, in his researches on the effect of diluents upon the illuminating value of hydrocarbons (*Chem. Soc. Journ.*, xlv., pp. 30 and 227), showed that ethylene, which was capable of developing a light of 68·5 candles power when burnt by itself, became non-luminous when diluted with about—

Hydrogen	90 per cent.
Carbon monoxide ..	80 ,,
Carbon dioxide	60 ,,
Nitrogen	87 ,,

results which all show that excessive dilution by inert gases destroys luminosity.

In order to see if dilution had the same effect upon acetylene, experiments were made by diluting it with pure hydrogen. The gases were mixed over water, the proportion of acetylene actually present in the gas being determined by analysis at the burner, as, although the water in both holder and meter was, as far as possible, saturated with the gas, yet, as the analyses show, the precaution was an important one.

Composition of Mixture.				Illuminating Value of Mixture per 5 c.c. when burnt in oo Bray.
Made in Holder.		At Burner.		
Hydrogen.	Acetylene.	Hydrogen.	Acetylene.	
90	10	90·5	9·5	Nil
80	20	81·5	18·5	1·8
70	30	65·5	34·5	14·0
50	50	43·5	56·5	87·0

Showing that dilution with between 80 and 90 per cent of hydrogen rendered the acetylene non-luminous when the mixture was burnt from a burner suitable for the higher values of gas.

In order to determine the point at which luminosity was destroyed when consuming the mixture in a burner suited to develope the light from a gas of low illuminating power, the experiment was repeated, using a 3-inch flame burning from the London argand, and also from a No. 4 Bray union jet, the latter being employed as it is difficult to determine the temperature in the argand flame.

Analysis of Mixture.		Illuminating Value per 5 cub. ft.	
Hydrogen.	Acetylene.	Argand.	No. 4 Bray.
92	8	Not measurable	
91	9	Not measurable	
88·5	14·5	4·1	1·7

So that luminosity would be destroyed in the argand by dilution with about 90 per cent hydrogen, and in the No. 4 Bray with about 88 per cent.

The next point to be determined was whether the destruction of luminosity in the diluted acetylene flame was in reality due to dilution, rendering it necessary to employ a higher temperature for the decomposition of the acetylene, or to other causes.

In order to do this, a tube made of specially infusible glass, 4 m.m. in diameter, was taken, and the Le Chatelier thermo-couple was fitted into it in the same way as before, used with the platinum tube, and all air having been rinsed out by a current of the mixture to be experimented with, the gas was allowed to pass at a steady rate of flow through the tube, the point at which the thermo-couple was situated being steadily heated by the Fletcher blowpipe, whilst the temperature recorded on the scale was noted the moment that incandescent liberation of carbon commenced.

Percentage Composition of Gas.		Temperature necessary to cause Deposition of Carbon with Luminosity.
Acetylene.	Hydrogen.	
100	0	780° C.
90	10	896
80	20	1000

It was found impossible to obtain a glass tube which would stand temperatures higher than this; but on plotting out the points so obtained, and which give a fairly straight line, it is seen that even if the increase in temperature only continues for increased dilution in the same ratio as shown in the experimental determinations, which is extremely unlikely, the reason of the destruction of luminosity in highly-diluted hydrocarbon gases is at once explained, as an increase of each 10 per cent in the dilution would necessitate an increase of 100° C. in the temperature of the flame, and with 90 per cent dilution a temperature of over 1700° C. would be required to bring about decomposition.

My reason for believing that it is highly improbable that when dilution is great it only requires the same increment in temperature to bring about decomposition as when the dilution is small is that in all the work I have done on the effect of diluents upon luminosity, and also in Prof. Percy Frankland's researches upon the same subject, dilution with hydrogen and carbon monoxide acts regularly, and decreases the value of the illuminant in a direct ratio down to about 50 per cent, whilst when the degree of solution exceeds 60 per cent a rapid falling away in the luminosity takes place, a fact which I think points clearly to a regular *pro rata* rise of temperature being needed for increase in dilution up to between 50 and 60 per cent. whilst higher degrees of dilution need a far greater rise of temperature in order to bring about decomposition.

Moreover, it would be manifestly incorrect to look upon the percentage of acetylene present in the gas issuing

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* A Paper read before the Royal Society.

from the burner as being any guide to the degree of dilution existing at the point at which luminosity commences. As the two small streams of gas issuing from the holes in the union jet meet and splay themselves out into the flat flame, they draw in with them a considerable proportion of air, the quantity being governed by the pressure of the gas at the burner.

This can be clearly seen by the fact that a high value gas which burns from a union jet burner of a given size with a smoky flame, under a gas pressure of half an inch of water, will burn with a bright, smokeless, and rigid flame of greatly increased illuminating value when the pressure is raised to 2 inches, whilst an ordinary coal-gas of 16-candle value must be burnt from a flat-flame burner at a pressure of about 0·75 inch if the best results are to be obtained, the increase in air drawn in, if the pressure rises to a much higher degree, diminishing the illuminating value.

Then, again, the area of non-luminous combustion in a mixture of gases like coal-gas means that some at least of the hydrocarbons are consumed before the required temperature for their decomposition is reached, whilst the products of combustion formed in the lower part of the flame are mixed with the flame gases, partly by diffusion and partly by being drawn into it by the upward rush.

When a simple hydrocarbon like ethylene or acetylene is burnt alone, the whole of the heat required to bring about the decomposition has to be generated by the combustion, without decomposition, of a considerable proportion of the hydrocarbon, and this means considerable dilution at the spot where the luminosity commences, so that at the top of a non-luminous zone of an acetylene flame there is only some 14 or 15 per cent of acetylene present, diluted with nitrogen, hydrogen, water vapour, and the oxides of carbon, whilst, with a mixture of 10 per cent acetylene and 90 per cent of hydrogen, in some cases little or no acetylene could be found at the top of the inner zone of the flame, it either having diffused with the hydrogen and been consumed, or polymerised to other compounds.

It is manifest that the luminosity of a flame will be governed, not by the percentage of acetylene in the gas, but at the point at which the temperature is sufficiently high to bring about decomposition.

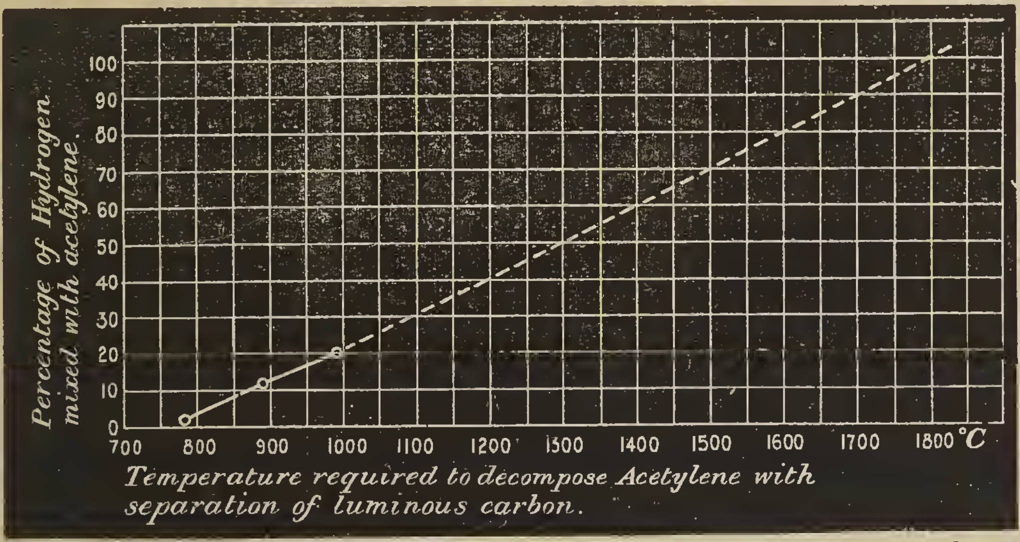

Fig. 1.

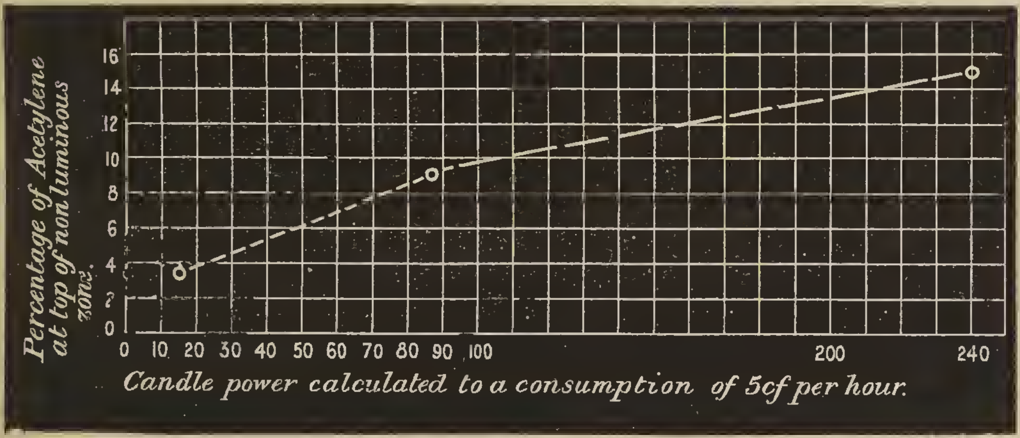

Fig. 2.

If, instead of making a mixture of 90 per cent hydrogen and 10 per cent acetylene, the hydrogen is burnt at the end of an open platinum tube, which has a fine platinum tube passing up the centre to the top of the inner zone of the flame, and if the acetylene be passed into the flame at the rate of one volume for every ten of the hydrogen, not only do we obtain an intensely luminous, but a very smoky flame.

In this experiment the gases were issuing from their respective tubes at the same pressure, but the small tube soon choked from deposited carbon, and it was found that the same results could be equally well attained by drawing down the inner tube to the level of the hydrogen tube, and making the acetylene issue at a slightly higher rate of flow, which hurried it in a compact stream through the inner zone of the hydrogen flame.

In order to see if the percentage of acetylene present at the top of the non-luminous zone bore any ratio to the illuminating value of the mixture, experiments were made in which mixtures of hydrogen and acetylene were burnt at a small flat-flame burner, and the percentage of acetylene was determined by gently aspirating out some of the flame gases from the top of the non-luminous zone.

Analysis of Mixture used.		Acetylene at top of Non-luminous Zone.	Illuminating Value of Flame for 5 cub. ft.
Hydrogen.	Acetylene.		
65·5	34·5	3·72	14·0
43·5	56·5	8·42	87·0
0·0	100·0	14·95	240·0

And on plotting out these results they certainly seem to point to the fact that, with flames of the same size burning from the same burner, the light emitted by the flame is directly proportional to the percentage of acetylene present at the top of the non-luminous zone of the flame, provided always that the temperature is sufficiently high to complete its decomposition.

(To be continued.)

SCIENTIFIC USES OF LIQUID AIR.[*]

By Professor DEWAR, M.A., LL.D., F.R.S.

When Faraday was working on liquid gases in this Institution about 1823, with such means as were then at his command, his inquiry was limited to the determination of specific gravities and vapour pressures of such bodies. Twenty years later, by the use of solid carbonic acid, the greatest cold then possible was obtained, and Faraday made admirable use of Thilorier's new cooling agent to extend his early investigations. Just as liquid carbonic acid produced in glass tubes was of no use as an agent for effecting the liquefaction of more resisting gaseous matters, until it could be manipulated in the solid state, so liquid air, until it could be handled, stored and used in open vessels, like any ordinary liquid, could not be said to possess scientific uses in any wide sense. Such operations become easy when double-walled vacuum vessels (such as were described in a former lecture) are employed in the conduct of experiments where substances boiling at very low temperatures have to be manipulated. The chief scientific use of liquid air consists in the facilities it gives for the study of the properties of matter at temperatures approaching the zero of absolute temperature. In this lecture the expression liquid air may mean either oxygen or air. Where a constant temperature is required oxygen is used. Liquid air made on the large scale may contain, after it is collected in open vacuum vessels, as much as 50 per cent of oxygen. Such a liquid boils between −192° and −182° C., and the longer it is stored the nearer it comes to −182° C., or the boiling-point of pure oxygen. For a number of experiments of a qualitative character, whether it is liquid air or oxygen that is used makes no difference. In many of the experiments to be recorded, liquid oxygen made from the evaporation of liquid air was employed. In pursuing this subject in consort with Professor Fleming,[†] a long series of experiments, involving the use of large supplies of liquid oxygen, have been carried out on the electric resistance of metals and alloys, and the results warrant the conclusion that at the zero of absolute temperature all the pure metals would be perfect conductors of electricity. Under such conditions a current of electricity started in a pure metallic circuit would develope no heat, and therefore undergo no dissipation. Similarly, we infer there would be no Peltier effect at the zero. In other words, the passage of electricity from one metal to another would take place without evolution or absorption of heat.

Further investigation, along with Professor Liveing,[*] on the refractive index of liquid nitrogen and air, has led to the conclusion that the refractive indices of nitrogen and air are respectively, for the D ray, 1·2053 and 1·2062. In these determinations, instead of using the prisms, we have employed the method of Terguem and Trannim, which consists in suspending in the liquid two plates of glass with a thin layer of air between them, and measuring the angle of incidence at which the chosen ray suffers total reflection at the surface of the air. As all the vacuum vessels are either spherical or cylindrical in form when filled with liquid, they act as lenses which are irregular and full of striations. Further, small bubbles of gas being given off in the liquid, rendered any image indistinct when viewed with a telescope. In order to avoid the necessity of observing any image through the liquid, it was used simply as a lens to concentrate the light observed on the slit of a spectroscope. Under such conditions the observations were easily executed and the results satisfactory.

For some time a series of observations on the thermal opacity of liquid oxygen and nitrogen have been projected. It is, however, exceedingly difficult to experiment in such a way as to eliminate the absorbing action of the glass vessels, and, as the use of rock salt is impracticable, the absorption of heat of low refrangibility remains for the present undetermined. It is possible, however, to use the glass vacuum vessels to determine approximately the relative thermal transparency for heat of high refrangibility, such as is radiated by a colza lamp. The following results represent the heat transmitted through the same vacuum vessels filled with different liquids, taking chloroform as the unit for comparison and correcting for differences of refractive index:—

Chloroform	1·0
Carbon bisulphide.. ..	1·6
Liquid oxygen	0·9
Liquid nitrous oxide ..	0·93
Liquid ethylene	0·60
Ether	0·50

From this result it follows that liquid oxygen is nearly as transparent to high temperature heat radiation as chloroform, which is one of the most transparent liquids next to carbon bisulphide. Liquid ethylene is much more opaque. These results must, however, be considered only as an approximation to the truth, and as generally confirmatory of the inferences Tyndall drew as to the relation between gases and liquids as absorbents of radiant heat.

Instead of silvering the interior and exterior of the vacuum vessels, it is found convenient when using mercury vacua to leave a little excess of liquid mercury, in order that the act of filling the inner vessel with liquid air should cause a fine silvery deposit of the metal over the exterior surface of the inner vessel. In such a vessel liquid air or oxygen shows no signs of ebullition, the surface remains as quiet and still as if it was ordinary water. The supply of heat is cut down to less than 4 per cent of what it is without exhaustion and silvering in good vacuum vessels. The result is that volatile liquids can be kept thirty times longer. Such vessels do not, however, maintain indefinitely the high standard of heat isolation they possess the first time they are used. After repeated use all vacuum vessels employed in the storage and manipulation of liquid air deteriorate. Illustrations of the appearance of such vessels are given in Figs. 1 and 2. The rapidity with which a space is saturated with mercury

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[*] A Lecture delivered at the Royal Institution, Jan. 19th, 1895.

[†] "The Electrical Resistance of Metals and Alloys at Temperatures Approaching the Absolute Zero." By James Dewar, LL.D., F.R.S., and J. A. Fleming, M.A., D.Sc., F.R.S., Professor of Electrical Engineering in University College, London. *Phil. Mag.*, 1892.

[*] "On the Refractive Indices of Liquid Nitrogen and Air." By Professors Liveing and Dewar. *Phil. Mag.*, 1893.

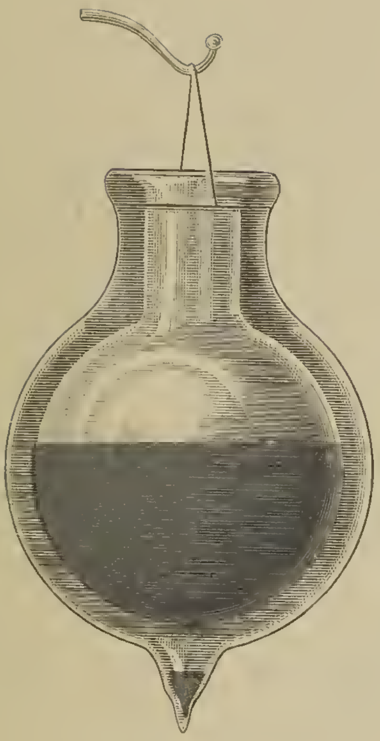

Fig. 1.

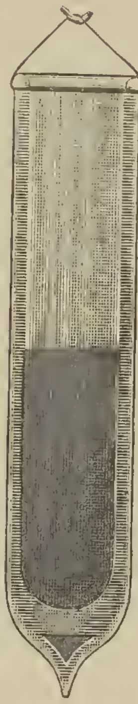

Fig. 2.

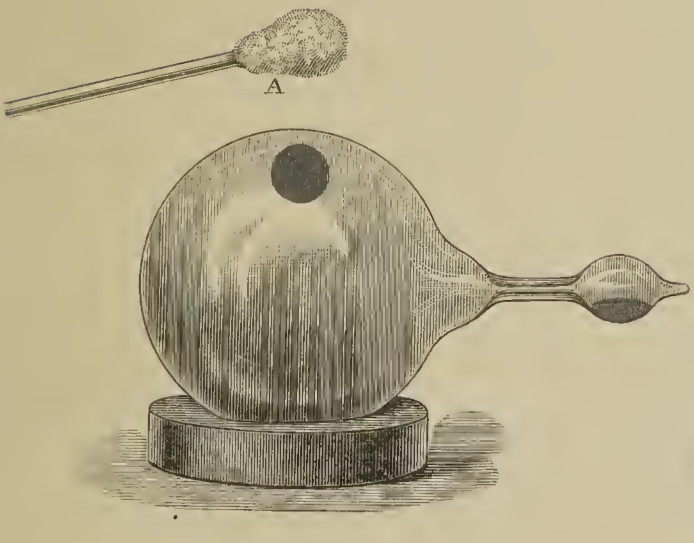

Fig. 3.

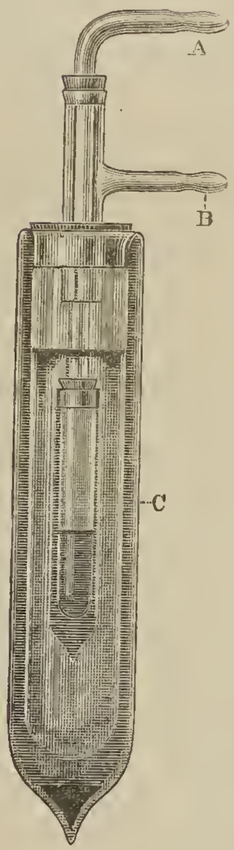

Fig. 4.

vapour (which we know exerts a pressure of about one-millionth of an atmosphere) is easily proved by simply filling a barometer in the usual way, and then instantly applying a sponge of liquid air to a portion of the glass surface of the Torricellian vacuum space, when a mercury mirror immediately deposits. It is important to know the amount of mercury deposited from a saturated atmosphere which is maintained (containing excess of liquid mercury) at the ordinary temperature, the condensation taking place when liquid air or oxygen is discharged into a vessel surrounded by such a Torricellian vacuum. If the deposit on the cooled bulb is allowed to take place for a given time, the outer vessel can then be broken and the amount of mercury which coated the bulb ascertained by weighing. Knowing the surface of the cooled bulb, the amount deposited per unit of area can be calculated. In this way it was found that in ten minutes 2 m.grms. of mercury per square c.m. of surface was deposited. Considering that one-tenth of a m.grm. of mercury in the form of saturated vapour at the ordinary temperature corresponds to the volume of 1 litre, this proves that the equivalent weight of 20 litres had been condensed in the space of ten minutes. This plan of cooling a portion of the surface of a vessel by the application of a liquid air sponge, enables us to test our conclusions as to the amount of matter present in certain vacua. Here is a globe of the capacity of 1 litre. It has been filled with, presumably, nothing but the vapour of mercury, by boiling under exhaustion and subsequent removal of all excess of liquid. Such a flask ought to contain mercury in the gaseous state that would weigh rather less than one-tenth of a m.grm., assuming the ordinary gaseous laws extend to pressures of less than one-millionth of an atmosphere. Now we know by electric deposition that one-tenth of a m.grm of gold can be made to cover one square c.m. of surface with a fine metallic deposit. Considering the general similarity in the properties of mercury and gold, we should therefore anticipate that if all the mercury vapour could be frozen out of the litre flask it would also form a mirror about one square c.m. in area. But after one such mirror is deposited, the renewed application of a second liquid air sponge to another portion of the surface would cause no visible deposit. This is exactly what takes place. If, however, two spheres, one much larger than the other, are joined together by means of a tube about 2 m.m. in diameter and 50 m.m. long, the whole space being a Torricellian vacuum (with some excess of mercury), then, on decanting, the mercury may be transferred to the smaller sphere, as is represented in Fig. 3. Now if an air sponge is applied to a portion of the surface of the larger sphere, a mercury mirror instantly deposits; but on applying a new air sponge to another portion of the surface, no further mercury mirror is formed. The narrow glass tube prevents the excess of liquid mercury in the small bulb supplying vapour rapidly to the larger one, so that the local cooling to – 180° C. of a portion of the surface has practically condensed all the mercury in the larger space, although the small one is still filled with saturated vapour and a free communication exists between them. If while in this condition the small bulb is inclined so as to allow a drop of liquid mercury to fall into the lower side of the large bulb, which has not been cooled, instant deposition of mercury takes place on the liquid air cooled portion of the upper surface. Under very small pressure of vapour, therefore, equalisation of pressure of two bulbs communicating by a narrow tube is a very slow process. There are cases, however, in which the application of a sponge of liquid air to the surface of a vessel causes no visible deposit, and yet the inference is that something has been condensed. The best arrangement to show this effect is to select highly exhausted vacuum tubes containing phosphorescent materials like alumina and other minerals, and to arrange the induction coil spark-gap of a little greater resistance than the vacuum tube. On starting the coil the current passes solely by the vacuum tube; but immediately the liquid air sponge cools a portion of the surface of the bulb, the discharge shifts to the air-gap. During the cooling the phosphorescence of the glass tube is greatly increased, but finally the resistance may become so great that all discharge in the vacuum tube ceases. Some old tubes belonging to the late Dr. De la Rue have given visible deposits near the electrodes, and in many the diameter and distribution of the striæ are materially changed during the local cooling to – 190° C. When large vessels containing nothing but mercury or iodine vapour as a residuum of the vacuum space are rubbed with a cotton-wool sponge of liquid air in a dark room, luminous glows filling the vessel take place occasionally, or bright flashes of light which enable the shape of the vessel to be seen. The ordinary mercury vacuum vessels show the same phenomena, which is doubtless due to electric discharges caused by friction and cooling.

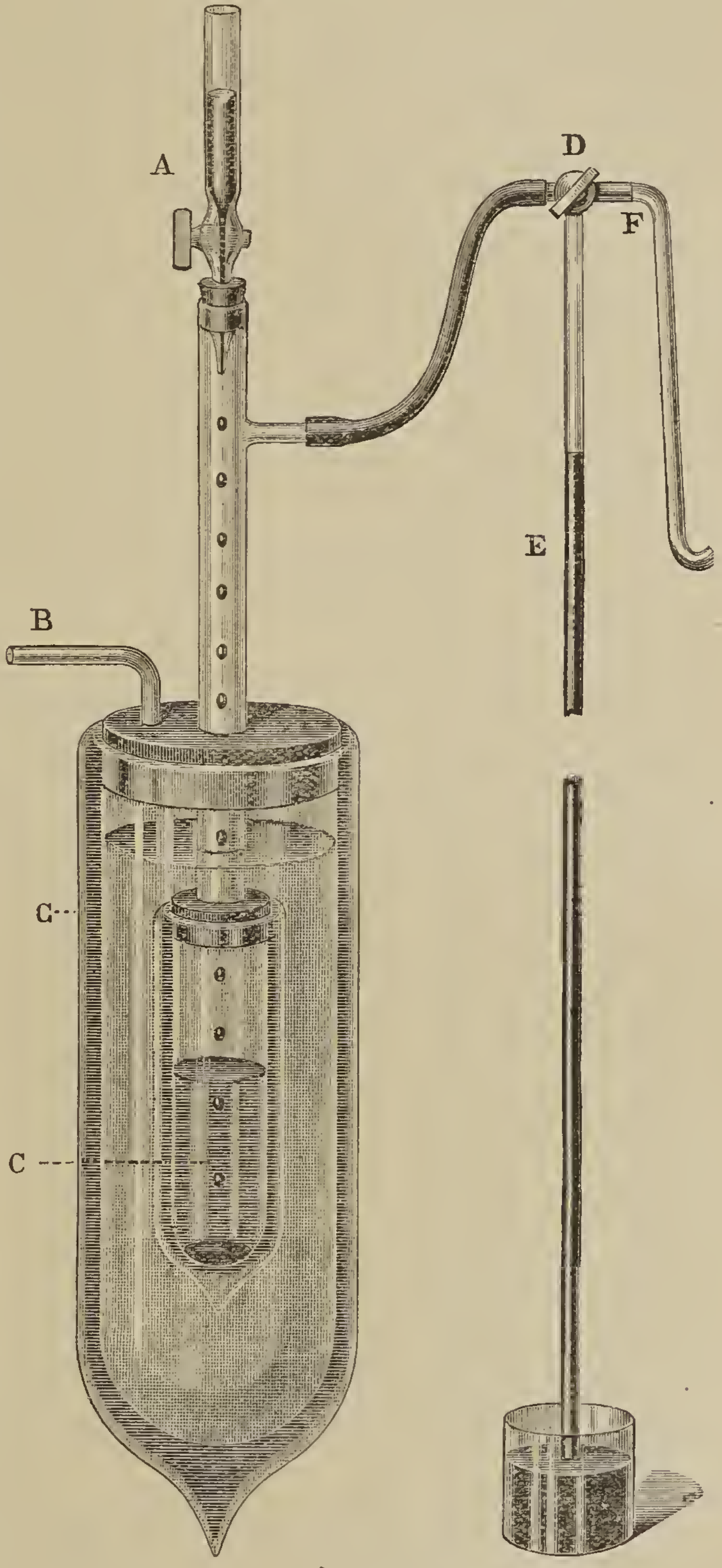

Fig. 5.

The optical properties of bodies cooled to the temperature of boiling liquid air will require long and patient investigation. An interesting fact easily observed is the marked change in colour of various bodies. Thus, for instance, oxide, sulphide, iodide of mercury, bichromate of potash, all become yellow or orange; while nitrate of uranium and the double chloride of platinum and ammonium become white. Chromic acid, dilute solution of iodine in alcohol, strong solutions of ferric chloride, and other coloured solutions, become greatly changed. Such facts are sufficient to prove that the specific absorption of many substances undergoes great changes at the temperature of −190° C.

The tranquil atmosphere of air above the surface of the liquid in cylindrical or spherical vacuum vessels is a convenient place to cool very fragile bodies. During the slow ebullition of the fluid, gas between −190° C. and −180° C. is given off, which has three times the density of ordinary air, and which falls slowly over the mouth of the vessel in a heavy stream. On dipping into this atmosphere small soap bubbles, they contract rapidly and then freeze. If a soap film is made on a circle of thin wire about 2 inches in diameter, and allowed to stand until it shows the various orders of coloured bands, and is then carefully dipped into the cool air, it freezes, showing all the original colours. The black band is, however, always broken. Speaking of films, an interesting experiment may be made with a thin stretched sheet of india-rubber, such as is used for making balloons. It is well known that stretched india-rubber contracts when heated and expands when cooled. Now this can be shown very easily by covering a glass funnel or the end of a cylindrical vessel with a stretched sheet of rubber as thin as the walls of balloons. Such a surface is quite flat and fairly transparent. If a sponge of liquid air is drawn across the surface, the course is marked by a series of wrinkles, due to the temporary expansion of the rubber caused by the extreme cold. The sheet of rubber, being extremely thin, soon regains the ordinary temperature, and the surface then is as flat and tense as before. During the continuous motion of the cotton-wool liquid air sponge over the rubber surface, it is followed by wave-like depressions which disappear almost as quickly as they are formed. The elasticity of india-rubber, after cooling to −182° C. and re-heating, seems unimpaired.

Organic substances that only become solid at very low temperatures may be divided into two classes—those which crystallise, and those which form glasses. Thus bisulphide of carbon, tetrachloride of carbon, methyl alcohol, hydride of amyl, all form crystals, whereas ethyl alcohol, amyl alcohol, turpentine, ethyl nitrate, chinoline, picolin, are glass-like. If a few drops of bisulphide of carbon are added to alcohol, and the mixture cooled to −180° C., a white solid emulsion is formed, whereas the addition of tetrachloride of carbon to the alcohol resulted in the production of a clear solid without any separation. In the same way pure methyl alcohol crystallises easily, but the addition of a few drops of ethyl alcohol prevents crystallisation and causes a glass to be formed. Thus the examination of the behaviour of organic bodies at low temperatures may be a fruitful means of organic investigation.

For many purposes of investigation it is necessary to keep liquid air without evaporation. This is readily done by the use of two vacuum test-tubes, fitting freely one inside the other, arranged as in Fig. 4. The smaller one is filled with liquid air, and, after the insertion of an india-rubber stopper and glass tube, is completely immersed in liquid air contained in the larger vacuum vessel. In the figure the tube A connects with the inner vacuum tube, and B with the outer. As the latter receives all the radiant and conducted heat, air is continuously boiling off through the tube B; but as the supply of heat is effectually cut off from the inner vacuum vessel, also containing liquid air, no air distils through tube A. This is the most convenient arrangement to use for the production of solid air. For this purpose B is connected with an air-pump until the pressure is reduced to about ½ inch, and therefore the temperature about −200° C. Then a good air-pump is put on to the inner vessel of liquid air (containing oxygen and nitrogen in the normal proportion of oxygen and nitrogen), by means of the tube A, while maintaining constantly the exhaustion in the outer vessel. In a short time the air in the inner vessel solidifies to a transparent jelly-like mass.

The same principle is used when the latent and specific heats have to be determined. Fig. 5 shows the general plan of the apparatus. Now a definite quantity of heat has to be conveyed into the inner vacuum vessel containing liquid air, with the object of finding the weight of liquid that distils off, on the one hand, or the elevation of temperature in the liquid that takes place on the other. For the purpose of adding a given quantity of heat it is convenient in some cases to use mercury (as represented in the figure), or to lower a piece of platinum or silver, or even glass, into the inner vessel: each unit of heat supplied evaporates a definite amount of air, which is readily ascertained by collecting the gas which comes off during the heat conveyance. In Fig. 5, A is the mercury, C the inner vessel of liquid air, D a three-way stopcock, F a tube for collecting the air given off; E is a barometric tube for observing the pressure when the inner vessel is exhausted. In a latent heat determination all that is necessary is to weigh the mercury added and to measure the amount of air by volume which has distilled from the liquid state. If the specific heat of the liquid is wanted, then the inner vessel is exhausted (as well as the outer) through the tube F to about ½ inch pressure, and the three-way stopcock turned so as to shut off F and connect the inner vessel with the manometer E. Mercury is now dropped into the inner vessel until the manometer rises to the atmospheric pressure or the liquid reaches its boiling-point under atmospheric pressure. Care must be taken to prevent the drops of mercury falling exactly in the same place, otherwise a mercury stalagmite grows up rapidly through the liquid, vitiating the results. Another objection to the use of mercury arises from the drops causing the rebound of small liquid air drops, which strike the cork and get evaporated away from the main body of liquid. The amount of mercury added conveys the necessary amount of heat needed to raise the given amount of liquid from its boiling-point under ½ inch pressure to its boiling-point under 30 inches. The relative pressures give the temperature range, and the weight of liquid air or other gas under observation is easily ascertained, together with the weight of mercury added. In this way the latent heat of liquid oxygen at its boiling-point is about 80 units, and the mean specific heat between −198° and −182° is 0·39

(To be continued).

ON THE
DETERMINATION OF TANNIC COMPOUNDS.
By AIMÉ GIRARD.

In 1882 (*Comptes Rendus*, xcv. p. 185) I published a process for the determination of the tannic compounds, which depends on the fixation of these compounds by an animal membrane of a definite and constant composition. This membrane consists of the intermediate coating of the intestine of the sheep,—a coating formed of pure muscular tissue, and which I obtained at first from the harmonic strings supplied in trade to musicians under the name of *violin ré*. This process has been repeatedly applied by various chemists, to whom it has yielded excellent results, whilst in the hands of others it has proved absolutely unsuccessful.

By occasion of a prolonged study of the composition of the grapes of the principal kinds of vines in France, undertaken two years ago by M. Lindet and myself,—the results of which we shall soon present to the Academy,—it has seemed necessary to resume the study of this procedure, and to search what can be the cause of success of some and the failure of others. I soon perceived that the cause must be sought in the unequal quality of the harmonic strings obtained in trade by the experimentalists.

At the time when I devised the process in question, M. Thibouville-Lamy kindly proposed for my purpose products of an exceptional purity. The chemists who have made use of my process have not always obtained specimens of a similar purity.

The intestines of sheep intended for the manufacture of fiddle-strings must be at first very carefully scraped on a die, to detach, on the one hand, the serous or peritoneal membrane, and, on the other, the mucous membrane, so as to lay bare the intermediate membrane formed exclusively of muscular fibres adhering together. It is then plunged into a solution of potassa, and treated sometimes with different reagents, and after being mechanically purified as just described, it is thus freed from fatty matter as completely as possible. At the same time it acquires such adhesive properties that if twisted with two or three similar membranes — spun, as it is technically called — it dries in the form of a solid cord, which constitutes a fiddle-string.

But without very special precautions, such as those adopted by M. Thibouville-Lamy, it is impossible to obtain under these conditions an animal membrane absolutely pure.

On examining with the microscope samples of the ordinary manufacture, even products already treated with care, I found that, adhering to the muscular tissue, there always remained some spots of the fatty tissue, whilst on the other hand the membranes, from the fact of their more or less prolonged maceration in an alkaline bath, in spite of repeated washings, retained always an important proportion of potassium carbonate and sulphate.

A number of specimens very carefully prepared gave the following results:—

	I.	II.	III.	IV.
Moisture	13·42	12·07	6·93	7·53
Fats	2·88	1·60	1·91	0·99
Soluble salts	10·56	10·46	5·01	6·10
Dry animal tissues ..	73·14	75·87	86·15	85·30

It is easy to understand that products thus loaded with impurities must in practice give bad results. The chemist must always present to the tanniferous liquid a known weight of animal tissue. But this tissue, if as impure as the foregoing samples, will give off to the water from 5 to 10 per cent of soluble salts; when tanned and dried at 100° to 105° it will lose 1 to 2 per cent of the fatty matter in the state of vapour; so that, in spite of the fixation of the tannin, its weight at the end of the analysis may be found less than the initial weight.

To avoid these errors it is sufficient to obtain strings carefully prepared in the ordinary manner, and complete their purification in the laboratory.

These membranes do not require to have been twisted in the form of fiddle-strings. If simply dried, and treated with sulphurous acid to ensure their preservation, will be fully sufficient for the determination of the tannic compounds.

The strings are then cut into threads of 0·15 metre in length, and submitted in the cold to the action of crystallisable benzene. These washings are repeated until the benzene no longer takes anything up. They are then exposed in the cold to the open air, and when the benzene has evaporated there follow three or four washings with cold distilled water.

When taken out of the water they are dried in cold air, moving them so that they may not cling together. They are then ready for use. All the causes of error are thus removed, and they may be safely used for the determination of the tannic compounds, according to the method described in 1882.—*Comptes Rendus*, cxx., 358.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1895.

Dr. Armstrong, President, in the Chair.

Messrs. George Thudichum and Arthur H. Coote were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Harold Allden Anden, B.Sc., 102, Acomb Street, Manchester; Lancelot Alexander Borradaile, B.A., Selwyn Coll., Cambridge; Henry Bradford, 21, Kensington Mansions, Earl's Court, S.W.; Irving Foster Hasslewood, The Elms, Aulaby Road, Hull; Robert Charles Marchant, 18, Westfield Park, Redland, Bristol; Henry F. A. Wigley, B.A., 64, Quentin Road, Lee, S.E.

Of the following papers those marked * were read:—

*32. "*The Volumetric Determination of Sugars by an Ammoniacal Cupric Solution.*" By Zdenek Peske. (Communicated by Professor Brauner).

Being dissatisfied with Fehling's method and its rather lengthy modification by Allen, and with the gravimetric method of Soxhlet-Allihn, the author tried to find a rapid and reliable process of estimating sugar based on Pavy's method of working in an ammoniacal solution. The latter method fails on account of the rapidity with which the reduced ammoniacal cupric solution is oxidised by the air. The author avoids this by covering the solution with a layer of paraffin oil of high boiling point ("white vaseline oil"). It is necessary to keep the amount of ammonia constant. The use of a current of indifferent gas was proposed to the author and tried by him some one and a half years ago, but was given up as the liquid rapidly loses ammonia, and its reducing factor is thereby so altered that constant results cannot be obtained. Tables are given showing the reducing power of a standard ammoniacal cupric solution (in presence of Rochelle salt) for liquids containing different amounts of (1) glucose, (2) invert sugar, (3) invert sugar in presence of cane sugar.

*33. "*The Action of Hydrogen Sulphide on Antimonic Acid Solutions.*" By Otto Bosek, Ph.D. (Communicated by Professor Brauner).

Berzelius, Rose, Rammelsberg, Bunsen, Willm, Thiele, and others, having obtained contradictory results, the question has been re-investigated.

The complete conversion of antimonious into antimonic compounds by the action of oxidising agents is difficult. Such agents as fuming nitric acid, potassium chlorate, and hydrochloric acid, and even bromine in alkaline solution, do not produce complete oxidation unless they act for a long time and are used in very large excess.

The experiments show the independent existence of compounds of the type SbX_4 (corresponding to the "antimonious acid" of Berzelius). The author has succeeded in obtaining a crystalline double salt of the tetrachloride $3KCl\cdot2SbCl_4$, and also the pure tetrasulphide Sb_2S_4, differing from either the trisulphide or the pentasulphide in its crystalline form and its highly characteristic pink colour.

An excess of an aqueous solution of hydrogen sulphide acting on antimonic acid solution at ordinary temperatures forms antimony pentasulphide, thus showing that exact results are obtained when Bunsen's directions are strictly followed.

When hydrogen sulphide acts on antimonic acid solutions, the quantity of antimony pentasulphide increases (*a*) the lower the temperature, (*b*) the more rapid the stream of hydrogen sulphide; while the quantity of antimony trisulphide mixed with sulphur increases (*a*) the the higher the temperature, (*b*) the slower the action of the hydrogen sulphide. The quantity of the pentasulphide formed increases up to a certain limit (10 to 20 per cent) with the amount of hydrochloric acid present, after which it diminishes. Antimonic solutions are more easily and completely reduced by hydrogen sulphide in presence of a chromic salt.

*34. "*Action of Hydrogen Sulphide on Antimonic, Arsenic, and Telluric Acids.*" By B. Brauner, Ph.D.

When antimonic acid and hydrogen sulphide interact, one or both of the changes represented by the following equations may take place—

$$(1)\ H_3SbO_4+5H_2S=Sb_2S_5+8H_2O,$$
$$(2)\ 2H_3SbO_4+5H_2S=Sb_2S_3+S_2+8H_2O.$$

At first a solution is formed which apparently contains a colloidal modification of the pentasulphide, possibly H_3SbS_4. When antimonic acid is heated with hydrogen sulphide in a solution containing much free hydrochloric or sulphuric acid, antimony pentasulphide is precipitated. Neither oxysulphantimonic acid nor any oxysulphantimonate corresponding with the analogous arsenic compounds could be obtained.

The more positive behaviour of antimony, as compared with arsenic, is in accordance with the relative positions of these elements in the periodic table.

In its behaviour towards hydrogen sulphide, telluric acid resembles arsenic acid more than antimonic acid, but no oxysulphotelluric acid could be isolated. It is known that antimony pentasulphide is decomposed into the trisulphide and sulphur when heated to 220°. The author finds that the same change occurs when the pentasulphide is exposed to sunlight, and when it is heated with water to 98°, the trisulphide separating in the black crystalline form.

*35. "*The Atomic Weight of Tellurium.*" By Bohuslav Brauner, Ph.D.

In continuation of his work on the determination of the atomic weight of tellurium, published in the *Transactions*, 1889, p. 382, the author has re-calculated the numerical data then obtained, and on reducing to a vacuum finds the number 127·71, which is higher by 0·86 than the atomic weight of iodine 126·85, whereas from its position in the periodic system tellurium should have an atomic weight between 123 and 125 On this account he is led to the conclusion that tellurium is not a simple substance, a conclusion which is supported by the following considerations:—1. Tellurium precipitated and dried in a current of an inert gas gives higher values for the atomic weight than when sublimed in hydrogen. 2. The properties and composition of the dibromide. 3. The varying results obtained on attempting the synthesis of the dioxide, the basic sulphate, and certain metallic tellurides. 4. The behaviour of tellurous and telluric acid solutions towards hydrogen sulphide.

A large quantity of tellurium was therefore carefully purified by the process described in the paper referred to above, and, after being converted into sodium sulphotellurate, was submitted to a process of fractional precipitation similar to that used for separating the rare earths from one another. On examining these fractions it was found that there were variations in the equivalent of the tellurium dioxide as determined by the permanganate method described in the *Transactions*, 1891, p. 238. This variation, however, was found to be caused by the presence of minute quantities of mercury, thallium, bismuth, copper, and lead in the extreme positive fractions, and of arsenic and antimony in the negative fractions. On the other hand, the tellurium obtained by further purifying the middle fractions showed scarcely any variation in molecular weight.

In the course of experiments on telluric acid, made with the object of controlling the determination of the atomic weight of tellurium, the author has found that it is very difficult to prepare the acid in a pure state; moreover, it behaves like a mixture of two substances. He has also discovered a new modification of telluric acid corresponding with the yellow tellurates, the existence of which was predicted by Berzelius.

The discovery of argon inclines the author to believe that it is one of a new group of elements (or a mixture of them) in the periodic system—the Argon Group—coming between the last two groups, and if it be assumed that tellurium is a mixture, or alloy, or compound of the true tellurium with Argon No. 4, or "Triargon," it would consist of equal parts (atoms) of the two,—

$$\frac{125\cdot4+130}{2}=127\cdot7,$$

and have the formula $Te_2A^4{}_2$.

*36. "*The Hydrolysis of Maltose by Yeast.*" By G. Harris Morris, Ph.D.

Until E. Fischer recently described (*Ber.*, 1894, 2985, 3479) experiments on the hydrolysing action of yeast on maltose, the opinion had been generally held that maltose is directly fermented by yeast, or that if hydrolysis take place, this phenomenon and that of fermentation occurred simultaneously, as it had never been possible to detect products of hydrolysis in a solution of maltose undergoing fermentation. Fischer has, however, shown that air-dried yeast and its extract, when digested with a solution of maltose, readily converts a very considerable proportion into dextrose, and also that the extract of moist yeast cells which had been ruptured by trituration with powdered glass possessed the same power. Moreover, in the second paper, he states that when unruptured yeast cells are digested with maltose solution for three days in presence of chloroform, some 40 per cent of that sugar is converted into dextrose. Fischer chiefly used pure cultures of Frohburg yeast in his experiments, but he also examined low-fermentation yeast, and pure cultures of other races, with similar results.

Having in view the important nature of the subject, and the bearing it has upon the determination of cane sugar in the presence of maltose by inversion with yeast, the author has repeated Fischer's experiments. He has obtained results confirming Fischer's statements as to the action of air-dried yeast and its extract, and also of ruptured moist yeast, but was quite unable to obtain any evidence of hydrolysis when moist and well-drained yeast was employed, although both pure cultures of Frohberg yeast and ordinary London brewery yeast were used. The experiments were made by digesting a 5 per cent solution of maltose with yeast (drained on a porous tile) in the proportion of 1 grm. of yeast to 100 c.c. of solution. The digestions were carried on for periods varying from twenty-four hours to three days at 35° C. in the presence of chloroform. The solutions were examined before and after the digestion, and dextrose was also tested for after digestion with phenylhydrazin acetate in the usual way. In all cases the optical and cupric reducing powers remained unaltered after digestion, and no trace of dextrose could de detected by the phenylhydrazin test. In order to further examine the question, maltose solutions were set to ferment, portions of the fermented liquid being withdrawn from time to time, and the matter remaining unfermented examined by the above tests. In no case was the slightest evidence obtained of the presence of dextrose, the analytical results showing the presence of maltose, and maltose only, in the fermenting solution.

In order to obtain some explanation of this remarkable difference in the behaviour of well drained but moist yeast, and of air dried yeast, a quantity of the former was digested with chloroform water for twenty hours, in order to kill the cells and then air-dried; any decomposition during drying, due to vital changes, was thus prevented. The dried yeast thus obtained possessed the same power as that dried in the ordinary way, and the author stated that Mr. F. W. Tompson had informed him that the yeast liquor, obtained as described in the paper of O'Sullivan and Tompson on invertase, which is manifestly a product of the decomposition of the yeast, and which possesses the power of inverting cane sugar to a most marked extent, was without action on maltose. That the action of dry yeast is not due to the cells being ruptured during powdering was shown by the fact that the horny mass remaining when yeast is dried on a porous tile was just as active when used in that form as when finely powdered before addition to the maltose solution.

The dry yeast has also the power of liquefying starch paste, and of producing dextrose from a starch-conversion from which all the soluble portions has been removed by repeated treatment with 80 per cent alcohol.

The author is making further experiments to ascertain the cause of the hydrolysing action of dry yeast.

37. "*Studies in Isomeric Change. Part IV. Ethylbenzene Sulphonic Acids.*" By GERALD T. MOODY, D.Sc.

In previous communications (*Proc. Chem. Soc.*, 1888, 77; 1892, 90, 213, 214) the author has called attention to the ease with which certain orthosulphonic acids of benzene derivatives undergo isomeric change, and are thereby converted into parasulphonic acids. The investigation has now been extended to the ethylbenzenesulphonic acids. The ethylbenzene available for these experiments was obtained from Kahlbaum, and was evidently impure, as, when shaken with sulphuric acid, it gave a bright red colouration, not due to free iodine.

As it has been stated by Chrustschow (*Ber.*, vii., 1166) that ethylbenzene on sulphonation gives rise to two distinct acids, it was considered desirable to sulphonate a highly purified specimen of the hydrocarbon. To obtain such, the crude product of sulphonation of Kahlbaum's ethylbenzene was converted into barium salt, which was several times re-crystallised and then converted into sodium salt. The latter was repeatedly re-crystallised until no doubt as to its purity could exist, and then hydrolysed. The hydrocarbon thus obtained, which boiled at 135°, was sulphonated both with chlorosulphonic acid and with sulphuric acid. With each of these sulphonating agents one, and only one, sulphonic acid, namely, ethylbenzeneparasulphonic acid, was obtained. This behaviour of ethylbenzene is remarkable when compared with that of methylbenzene, which is known to give rise to a large proportion of ortho-acid on sulphonation. Ethylbenzeneparasulphonic acid forms a well-characterised barium salt which is anhydrous and does not contain 1 mol. of water of crystallisation, as stated by Sempotowski (*Ber.*, xxii., 2662), and a sodium salt which crystallises with $\frac{1}{2}$ a molecular proportion of water. The sulphonic chloride solidifies in a freezing mixture and melts at 12°; the sulphonamide crystallises from water in needles, from alcohol in six-sided plates, and melts at 110°.

In order to obtain ethylbenzeneorthosulphonic acid, ethylbenzene was brominated and the resulting bromoethylbenzene sulphonated and coverted into barium salt. The less soluble barium salt which crystallises in characteristic, long, shining plates, is a derivative of parabromethylbenzeneorthosulphonic acid. It contains 3 mols. of water of crystallisation, and yields a beautiful sodium salt. The latter, on reduction with zinc-dust and sodium hydroxide, yields sodium ethylbenzeneorthosulphonic acid, which crystallises with 1 mol. of water. The orthosulphonic chloride is an oil; the orthosulphonamide melts at 97°. The acid obtained on heating the sulphonic chloride with water at 140° crystallises in white, deliquescent prisms. When it is heated at 100°, either in a tube through which a current of dry air passes, or in an open dish, it is rapidly converted into the para-acid. This change is unaccompanied by the liberation of more than a mere trace of sulphuric acid.

(To be continued).

Some New Combinations of Hexamethyleneamine. —M. Delépine.—The author describes the two chloromercurates, the double mercurate of hexamethyleneamine and ammonium, the iodo-mercurate, and the action of the phenylhydrazine hydrochlorate.—*C. R.*, cxx., No. 13.

NOTICES OF BOOKS.

On the Influence of Copper on Cast-Iron, Iron, and Steel. By V. LIPIN, Mining Engineer, Chief Metallurgist of the Poutiloff Works. 69 pages (in Russian). St. Petersburg. 1895.

UNDER this heading M. Lipin has published a very interesting investigation. The objection to copper in iron and steel works, as is known, is exceedingly great.

By many careful experiments, elaborately conducted by M. Lipin at the extensive Poutiloff Works, the investigator has come to the definite conclusion that, though it is certainly not desirable for iron or steel to contain noxious elements, yet the presence of copper may be safely tolerated up to 0·5 per cent in wrought-iron and up to 1—2 per cent in cast-steel. Such metals behave in the same manner as material free from copper.

M. Lipin also reasonably remarks that many rich iron-ores, now lying idle only on account of containing 0·475 per cent of copper, in an oxidated form, could be safely used for the manufacture of cast-iron.

OBITUARY.

PROFESSOR LOTHAR VON MEYER.

WE regret to have to announce the death of Lothar von Meyer, Professor of Chemistry at the University of Tubingen, at the age of sixty-five. His decease is a considerable loss to science. He chiefly devoted his attention to the study of physiological and theoretical chemistry, and in both branches he contributed to an increased knowledge of the subject. His most important work, in which he developed his views on chemistry in general, is entitled "The Modern Theories of Chemistry."

PROFESSOR DANA.

PROFESSOR JAMES DWIGHT DANA, the eminent mineralogist and geologist, died on the 15th inst. of heart failure. He had been Professor of Natural History and Geology at Yale College since 1855, and was a Fellow of the Royal Society of London, as well as member of the French Academy and of other scientific bodies in Europe.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 13, April 1, 1895.

Composition of the Water of Field Drains.—P. P. Dehérain.—The nitrogen which the crop does not take up in a bad season is carried off in the drainage. The losses from bare lands are infinitely greater than those from lands under crops. Hence the soil should be covered with vegetation as long as possible.

Prof. Ramsay, who was present at the sitting, gave verbally some account of the results which he has recently forwarded to the Academy, and which have already been inserted.

On a Radiometer of a Symmetrical Construction, Rotating by the Action of a Dissymmetric Illumination.—G. Seguy.—We have here a case of re-discovery, such a radiometer having been described by Mr. Crookes as far back as 1876.

Thermic Study of the Anhydrous Barium and Strontium Iodides.—M. Tassilly.—Formation-heat of solid BaI_2, setting out from its elements (x representing the oxidation-heat of barium:—Ba solid + I_2 gaseous = $x + 13{\cdot}7$ cal.; Ba solid + I_2 solid $x + 2{\cdot}9$ cal. Formation-heat of solid SrI_2 setting out from its elements:—Sr solid + I_2 gaseous + 123·1 cal.; Sr solid + I_2 solid + 112·3 cal.

Properties of the Nickel and Cobalt Salts.—M. de Koninck.—A reclamation of priority concerning the properties of the nickel and cobalt sulphides.

Calcium and Barium Alcoholates.—M. de Forcrand.—A thermo-chemical paper not adapted for useful abstraction.

Ammoniated Bases derived from Hexamethyltriamidotriphenylmethane and their Action on the Rosanilines.—A. Rosenstiehl.—According as a phenylic carbinol is amidated or ammoniated (in para) the alcoholic function is modified. In the amidated substances the alcoholic function comes first into play. In the ammoniated substances, on the contrary, the ammonium function is the first to act, and the alcoholic hydroxyl no longer reacts with the acids, but still reacts with the alcohols to form mixed ethers. When the same mol. contains nitrogen in two states of saturation, the function of the ammoniated base predominates still over the aminic and the alcoholic function. But there is a moment of hesitation between the two latter. The aminic function comes into play before the alcoholic function, though only in a transitory manner, and when an equilibrium is established by time, or by the intervention of heat, the alcoholic function still predominates over that of the double amine.

MEETINGS FOR THE WEEK.

MONDAY, 22nd.—Society of Arts, 8. (Cantor Lectures). "Recent American Methods and Appliances employed in the Metallurgy of Copper, Lead, Gold, and Silver," by James Douglas.
—— Medical, 8.30.
TUESDAY, 23rd.—Royal Institution, 3. "Alternating and Interrupted Electric Currents," by Professor George Forbes, F.R.S.
—— Society of Arts, 8. "Art of Casting Bronze in Japan," by William Gowland.
—— Institute of Civil Engineers, 8.
—— Medical and Chirurgical, 8.30.
—— Photographic, 8.
WEDNESDAY, 24th.—Society of Arts, 8. "The Use of Electricity for Cooking and Heating," by R. E. Crompton, Pres. Inst. Elect. Eng.
—— British Astronomical Association, 5.
—— Geological, 8.
THURSDAY, 25th.—Royal, 4.30.
—— Society of Arts, 4.30. "The Coming Railways of India, and their Prospects," by J. W. Parry, A.M.Inst.C.E.
—— Royal Institution, 3. "The Liquefaction of Gases," by Prof. Dewar, F.R.S.
—— Institute of Electrical Engineers, 8.
—— Chemical, 8. "The Action of Nitrosyl Chlorides on Amides," by Prof. Tilden, F.R.S., and Dr. M. O. Forster. "The Action of Nitrosyl Chloride on Asparagine and Aspartic Acid: Lævo-rotatory Chlorosuccinic Acid," by Prof. Tilden, F.R.S., and H. J. Marshall. "On a Property of the Non-luminous Atmospheric Coal-Gas Flame," by L. T. Wright. "A Constituent of Persian Berries," by A. G. Perkin and J. Geldard. "Potassium Nitrosulphate," by E. Divers, F.R.S., and T. Haga. "Di-ortho-Substituted Benzoic Acids," "Hydrolysis of Aromatic Nitriles and Acid Amides," and "Action of Sodium Ethylate on Deoxybenzoin," by J. J. Sudborough, Ph.D.
FRIDAY, 26th.—Royal Institution, 9. "The Effects of Electric Currents in Iron on its Magnetisation," by John Hopkinson, F.R.S.
—— Physical, 5. "A Theory of the Synchronous Motor," by W. G. Rhodwell. "Note on a Simple Graphic Interpretation of the Determinantal Relation of Dynamics," by G. H. Bryan.
SATURDAY, 27th.—Royal Institution, 3. "English Music and Musical Instruments of the 16th, 17th, and 18th Centuries," by Arnold Dolmetsch.

THE CHEMICAL NEWS.
Vol. LXXI., No. 1848.

SCIENTIFIC USES OF LIQUID AIR.*

By Professor DEWAR, M.A., LL.D., F.R.S.

(Concluded from p. 194).

Seeing that the most powerful chemical affinities are in abeyance at very low temperatures, it is a matter of great interest to ascertain what change comes over the physical force we name cohesion. Here we are dealing with the molecular forces which are effective in uniting together the particles of solid bodies, in contrast to the force we name chemical attraction, which exists most characteristically between dissimilar molecules. Both are alike in this respect, that they are insensible at sensible distances. If we accept the theory of matter which regards finite heterogeneousness of the most homogeneous bodies as proved, then Lord Kelvin has shown that gravitation alone would account for the so-called cohesive forces. Thus, he says ("Popular Lectures," vol. i., p. 60):—"But if we take into account the heterogeneous distribution of density essential to any molecular theory of matter, we readily see that it alone is sufficient to intensify the force of gravitation between two bodies placed extremely close to one another, or between two parts of one body, and therefore that cohesion may be accounted for, without assuming any other force than that of gravitation, or any other law than the Newtonian." Another view of the cohesive forces is taken by Mr. S. Tolver Preston, in his work entitled "Physics of the Ether," p. 64. He says, "The phenomena of 'cohesion,' 'chemical union,' &c., or the general phenomena of the aggregation of molecules, being dependent on the molecular vibrations as a physical cause, it would therefore be reasonable to conclude that variation of vibrating energy (variation of 'temperature') would have a most marked influence on these phenomena, as is found to be the fact. Further, since when a physical cause ceases to exist the effect also ceases, it follows that at the absolute zero of temperature (absence of vibrating energy) the general phenomena of 'cohesion,' including the aggregation of molecules in chemical union, would cease to exist." If this theory is pressed so as to include the gaseous state, then at the temperature of −274° C. we may imagine the particles reduced to an incoherent layer of dust or powder. The experimental facts do not, however, warrant this conclusion, seeing that at the lowest temperature reached, which is about −210° C., air remains a transparent jelly. That a low temperature causes profound changes in the elastic constants of a metallic body is most easily shown by placing a rod of fusible metal in liquid air, and comparing the deflection produced by a weight when the rod is supported at one or both ends before and after cooling.

The Young modulus is increased to between four and five times its amount at ordinary temperatures. In the same way, the rigidity modulus can be shown to be greatly changed by cooling a spiral spring made of fusible metal wire. Such a spring at the ordinary temperature is quickly drawn out into a straight wire, by attempting to make it support an ounce weight. The same spiral, cooled to −182° C., will support a couple of pounds, and will vibrate like a steel spring so long as it is cool. In the same way, a bell or tuning-fork of fusible metal gives a distinct metallic ring at −180°. If two tuning-forks are taken of identical pitch, and one cooled to −182°, then on simultaneously striking them beats are very distinctly heard. The simplest plan of getting some idea of the change in the cohesive force at low temperature, is to ascertain the tenacity or breaking stress of the metals and alloys under such conditions, and to compare such results with similar experiments made at the ordinary temperature with the same metallic samples, using the same apparatus. In this way the comparative values are reliable. The only difficulty is the large quantity of liquid air or oxygen required to cool the steel supports of the wires, which have to be broken. Seeing that wires less than 1-10th inch in diameter are unreliable, good strong rigid steel supports are needed, and, as these have to be cooled each time a wire is broken, the experiments involve large quantities (gallons) of liquid air and oxygen. Further, as not less than three, and in many cases six experiments must be made with each sample of wire, and the stress in each case can only be applied slowly, work of this kind extends over long periods of time, and this means increased waste of liquid gases. Fig. 6 shows the general plan of the part of the testing-machine which supports the wires

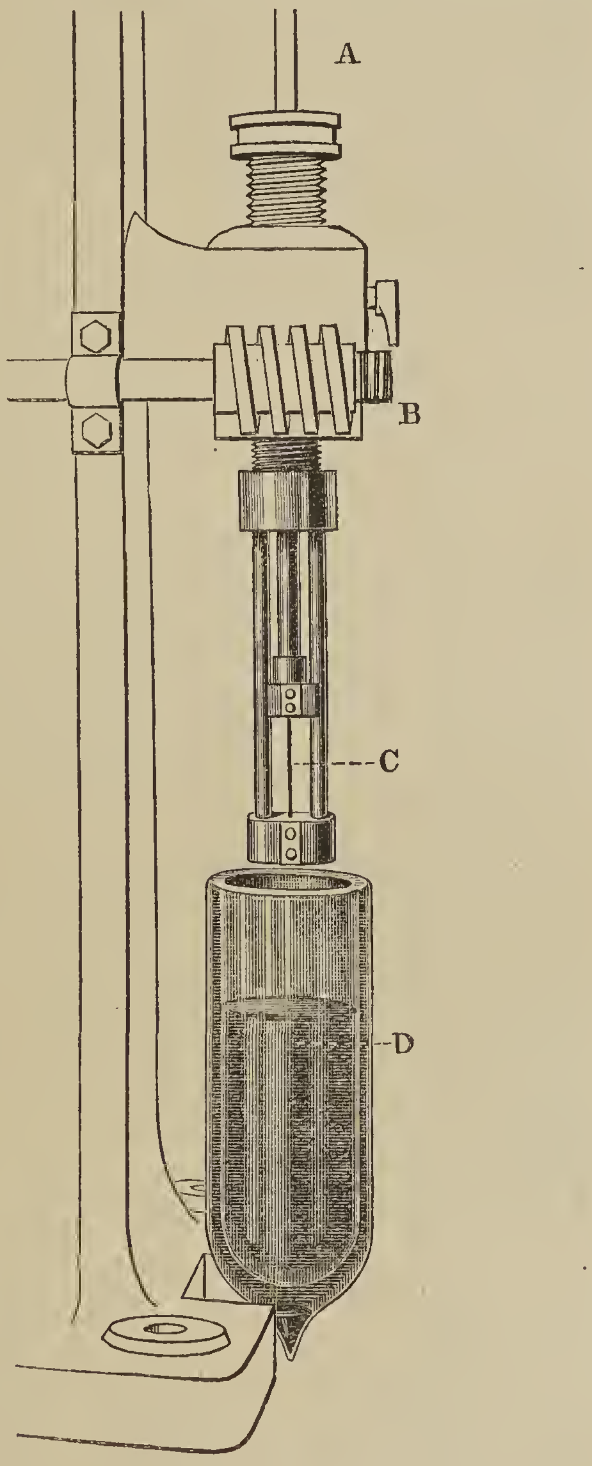

Fig. 6.

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* A Lecture delivered at the Royal Institution, Jan. 19th, 1894. (By an error this date was given in our last number as 1895, instead of 1894).

which have to be broken. In the figure, A is the steel rod which is connected to the multiplying levers, the stress being gradually increased as usual by running in water into a vessel hung from the long end of the lever; C is the wire to be tested, B is an arrangement which measures roughly the extension of the wire, and D is a large silvered vacuum vessel holding the liquid oxygen. This latter vessel must be large, in order to avoid any part of the supports of the wire coming into contact with the sides, otherwise the shock of the wire on breaking shatters the vacuum bulb. The rupture must be made while the wire is immersed in the liquid oxygen, and the whole of the supports thoroughly cooled down. The wires must be caught in long V-shaped grooves made in the steel supports in order to avoid slipping, and change in the cross section of the wire. As a rule, the wires used were $\frac{1}{10}$ inch in diameter and 2 inches long. The following table gives the mean results of a large number of experiments:—

Table I.—*Breaking Stress in Pounds of Metallic Wires* 0·098 *Inch Diameter.*

	15° C.	−182° C.
Steel (soft)	420	700
Iron	320	670
Copper	200	300
Brass	310	440
German silver	470	600
Gold	255	340
Silver	330	420

An inspection of this table proves that all the common metals and alloys increase in tenacity at low temperatures: thus iron has doubled its breaking stress, and the other metals and alloys are all increased from a third to a half the normal amount. This increase of strength is solely due to the low temperature, and persists only during its continuance. Wires that have been cooled to the temperature of −182° C., and allowed to regain the ordinary temperature, are in no way changed as regards their breaking stress.

A second series of experiments were made with a set of cast test-pieces of metals and alloys. The test-pieces, all cast in the same mould, were 2 inches long with ½-inch spherical ends, the cylindrical portion being $\frac{2}{10}$ inch diameter. The spherical ends of the test-pieces rested in similar cavities made in a special set of steel supports that fitted on to the testing-machine. Crystalline metals give castings that are far from uniform one with another, and it is very difficult to get even comparable results with metals like zinc, bismuth, and antimony. The following table gives the experimental results:—

Table II.—*Breaking Stress in Pounds of Cast Metallic Test-Pieces. Diameter of Rod* 0·2 *Inch.*

	15° C.	−182° C.
Tin	200	390
Lead	77	170
Zinc	35	26
Mercury	0	31
Bismuth	60	30
Antimony	61	30
Solder	300	645
Fusible metal (Woods)	140	450

It will be noted that in this list the breaking stress, by cooling to −182° C., has been increased to three times its usual value in the case of fusible metal, and to twice its usual value in the case of tin, lead, and solder. The results with zinc, bismuth, and antimony are exceptional, seeing they appear to be diminished in tenacity. This, however, may be only apparent, because the stresses set up in cooling such highly crystalline bodies probably weaken some set of cleavage planes so that rupture is then comparatively easy. In any case it must be admitted that no reliance can be placed on the tenacity of highly crystalline metals. The breaking stress of mercury is interesting, and turns out to be at −182° C. nearly half that of lead at the ordinary temperatures. The percentage elongation is not given in the foregoing tables, simply because the value of such measurements is of little importance when such short pieces of the metals are under observation. The general results of such observations are, however, interesting: thus lead and tin at ordinary temperatures elongate before breaking about the same amount, whereas if tin is cooled to −182° C. it hardly shows any extension, and lead under such conditions shows no change, stretching as much at −182° as at 15° C. Solder and fusible metal stretch less, and the cross section of the break is much less at −182° than at 15° C. The above experiments can only be considered as preliminary to a more elaborate investigation of the actual variation of the elastic constants at low temperatures. It will require complex experimental arrangements to get reliable measurements of the Young modulus and the rigidity modulus at the temperature of boiling liquid air. In the case of fusible metal, a first attempt to compare the ratio of the Young modulus at 15° and −182° with the ratio of the rigidity modulus between the same limits of temperature, has resulted in finding that both constants are increased in the same proportion. From this it would follow that the resistance to compression of the substance at −182° C. must be increased in a similar ratio. The comparative behaviour of strong steel spirals at 15° C. and −182° as to their elongation on the repeated addition of the same load was a subject examined on several occasions. The most careful comparison of such spirals, however, revealed no measurable differences in their elongation between the ordinary temperature and that of boiling oxygen. This may be due to the want of sufficient sensibility in the testing-machine when applied to such delicate experiments. In the meantime it is reasonable to conclude that the rigidity modulus of very hard steel is not much changed by cooling it to −182° C. If balls of iron, tin, lead, or ivory are cooled to −182° C., and dropped from a fixed height on a massive iron anvil, the elastic rebound is markedly increased in all cases. The flat distortion surface produced on the lead sphere after impact is only one-third the diameter of the circular surface produced at the ordinary temperature when the lead ball falls from the same height.

The examination of the magnetic condition of matter at low temperatures is a subject of great interest and offers a wide field for investigation. In a former lecture the magnetic properties of liquid oxygen and air were discussed. Owing to the experimental difficulties, accurate quantitative measurements of the permeability have not yet been successful. Faraday was the first experimenter who examined the magnetic condition of matter at the lowest temperature that could be commanded in his time, viz., about −110° C. He did not succeed in making any substance which was non-magnetic at ordinary temperatures assume the magnetic state at the lowest temperature of the solid carbonic acid ether bath *in vacuo*. Later experimenters have directed their attention more especially to the action of high temperatures on magnetism, and the work of Professors Hopkinson and Ewing in this field of research is well known. Professor Trowbridge examined the effect of a temperature of −80° C. on a permanent magnet, and came to the conclusion that the magnetic moment was diminished by about 50 per cent. Professor Ewing found that an increase of temperature of 150° C. above 10°, caused a reduction of the magnetic moment of a bar magnet by about 40 per cent, and that the magnet on cooling recovered its original state. This result would lead us to expect that if the same law is followed below the melting-point of ice as Ewing found above it, then a bar magnet cooled to −182° C. ought to gain in magnetic moment something like 30 to 50 per cent. The experiment of Professor Trowbridge is, however, apparently opposed to such an inference. It appears, however, that Professor Trowbridge cooled a magnet that had not reached a constant state (that is to say, one that on heating would not have completely recovered its magnetisation on cooling), because after the magnet had been cooled to −80° on regaining the ordinary temperature, it had lost 50 per cent of its original magnetic moment. Such a magnet would apparently diminish in magnetic moment on cooling and heating the first time the action was examined, but a repetition of the process when the action of magnetisation and temperature were strictly reversible might lead to an opposite conclusion. To settle this question a series of experiments on the magnetic moment of small magnets cooled to −182° were carried out. Small magnets from half an inch to an inch in length were made of watch-spring or steel wire and were either used separately or in bundles; they were fixed rigidly in a block of wood by means of copper staples, and in this condition were easily clamped firmly in the field of a magnetometer. The cooling was effected by applying a cotton-wool sponge of liquid air. The relative deviations of the magnetometer are proportional to the magnetic moment of the magnet under the respective conditions of +15° and −182° C. After the first cooling the magnet is allowed to regain the ordinary temperature, and the operation of cooling and heating is repeated three or four times. The following table gives some of the results, and these may be taken as typical of a large additional number unrecorded.

If the experiment marked (1) is examined we find cooling to −182° in the first cycle produced no change of magnetic moment, but that on heating to +15° C. the magnet had lost 30 per cent of the original strength. In the second cycle cooling increased the magnetic strength of the magnet, in the condition in which it is left after the first cooling by 33 per cent, and heating diminished it by 5 per cent; whereas in the third cycle cooling showed 36 per cent increase and no loss in heating. It was only after three alterations of temperatures from +15° to −182° C. that the magnet reached a steady condition. In experiment (3) the first cooling shows a loss of 24 per cent, while in experiment (4) the first cooling shows a gain of 12½ per cent.

Change of the Magnetic Moments of Permanent Magnets at +15° and −182° C. per cent of the Value at the beginning of each Cycle, which is always 15°.

	−182° C.	+15° C.
(1) Hard steel, 0·5 inch long and 0·4 inch diameter—		
First cycle	+0	−30
Second ,,	+33	−5
Third ,,	+36	0
(2) Soft steel—		
First cycle	+12	−28
Second ,,	+51	0
Third ,,	+51	0
(3) Hard steel, 1·03 inch long, 0·4 diameter—		
First cycle	−24	−43·4
Second ,,	+23	0
Third ,,	+23	0
(4) Nine steel wires in bundle—		
First cycle	+12·5	+3
Second ,,	+38	−2
Third ,,	+33	0
Tested four days after—		
First cycle	+50	0

It is clear, therefore, that according to these experiments, every magnet has individual characteristics that may either result in no change on cooling or the addition or subtraction of from 12 to 24 per cent in the magnetic strength. All the experiments, however, show that a repetition of the cycle of heating and cooling brings the magnet to a steady state, in which cooling always causes increase in the magnetic strength of from 30 to 50 per cent, and the re-heating brings about no loss in the original magnetic moment. Such a marked alteration of magnetic strength might be used as a thermometer in low temperature research, and it is my intention to extend the enquiry to the lowest temperature that can be reached by the evaporation of nitrogen in vacua. A simple mode of showing the sudden alteration of magnetic strength on cooling is to surround a permanent magnet made up of a bundle of steel wires with a coil of copper wire, leaving the ends of the magnet to project so that they can be dipped in liquid air. When the copper wires are attached to a galvanometer, and one of the ends of the magnet cooled, an induced electrical current occurs, due to the sudden magnetic change. Accurate observations must be made on the permeability and susceptibility of the magnetic metals at the temperature of boiling liquid air, and the above results are an indirect guarantee that this field of investigation will be fruitful in new scientific facts.

This lecture has already covered a very wide field. It is easy to put into a Friday evening discourse the work of a year. Members and friends have chiefly contributed to the Research Fund, which has enabled the Institution to extend the experimental plant needed for the prosecution of research in this field of enquiry, and they have strong claims to learn, in the first instance, the results of the general laboratory work. My object has been to illustrate the scientific uses of liquid air. To do this with any satisfaction requires what may be called a good deal of scientific prospecting. It is one thing to discover where the ore lies, it is another thing to produce the refined metal. Investigations on the properties of matter at the temperature of boiling liquid air, must be in the first instance rather qualitative than rigidly quantitative. In my opinion scientific progress is best served by conducting the enquiry on these lines. It will be easy to refine later on.

I have to acknowledge the great assistance I have received in the conduct of these experiments from my excellent chief assistant, Mr. Robert Lennox, and I must also express commendation of the way Mr. Heath has helped in the work.

TERRESTRIAL HELIUM ?

Professor J. Norman Lockyer, F.R.S., writes in the current number of *Nature* as follows:—

"I have received the following letter and enclosure from Prof. Thorpe:—

"'University of Glasgow, April 16.

"'My dear Lockyer,—The enclosed extract from a letter just received from Clève of Upsala may be of interest to you.

"'Ever yours,
"'T. E. Thorpe.'"

"'I have got from Mr. Crookes a letter in which he informs me that the gas in Clèveite contains the long-searched for helium.

"This letter arrived exactly the very day one of my pupils, Mr. Langlett, tried to get the gas of Clèveite in my laboratory. The gas given off from my mineral did not contain a trace of argon. The spectrum has been examined by Thalén, who found an exact coincidence of the line of the gas with the helium line and besides some others:—

Wave-length.	Intensity.
6677	Half-strong
5875·9	Strong: helium
5048	Half-strong
5016	Strong
4922	Half-strong
4713·5	Weaker.

“ ‘I have sent a letter about it to Berthelot. If you like, you may communicate the result to the Chemical Society, Mr. Ramsay, Crookes, and other friends. . . . An experiment to determine the specific gravity did not give satisfactory results, but seems to indicate that it is a very light gas, still more heavy than hydrogen. Will this gas fill the gap between hydrogen and lithium? It will become very interesting to see. What makes me much curious is, that our helium gas was free from argon, and that Mr. Ramsay's (according to *Comptes Rendus*) did contain that curious stuff. Is there any relation between argon and helium, and are we facing a new epoch in chemistry?’

“Although my results are not yet complete for publication, the foregoing communication makes it desirable that I should state at once that immediately on the publication of Prof. Ramsay's statement, by the kindness of Mr. L. Fletcher I was enabled to study the gases given off by Clèveite by heating *in vacuo*, a method I have used for metals and meteorites.

“A very small quantity of Clèveite is all that is necessary to obtain a considerable volume of the new gas, which comes off associated with hydrogen.

“I have now examined several tubes. I have found no argon lines; I have not found the lines, other than the yellow one, given by Crookes; but lines have been recorded near some of the wave-lengths given by Thalén, especially the one at 6677, near a line I discovered in the chromosphere in 1868. So far the sky has not been clear enough to enable me to determine by direct comparison with the chromospere the position of the line in the yellow with great dispersion.”

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending March 31st, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, April 10th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 167 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily as far as possible, from March 1st to March 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 167 samples examined four were recorded as “clear but dull,” the remainder were clear, bright, and well filtered.

With the improved meteorological conditions the London waters are approaching a state of considerable purity. In our report for the month of March last year we commented on the then excellent quality of the waters, and said that they were “rapidly approaching their high summer standard.” The following comparison between the present month's supply and that of March, 1894, will show that the former high degree of analytical purity has been more than maintained.

Comparison of the Averages of the Five Thames-derived Supplies for the Months of March, 1894 *and* 1895.

	Common Salt. Per gall. Means.	Nitric Acid. Per gall. Means.	Hardness. Degrees. Means.	Oxygen. reqd. Per gall. Means.	Organic Carbon. Per gall. Means.	Colour. Br'n: Blue. Means.
Mar., 1894	2·285	1·101	15·32	0·052	0·121	21·3 : 20
,, 1895	2·130	0·937	15·12	0·043	0·117	18·2 : 20

Bacteriological examinations have been continued throughout the month, the process adopted being identical as regards culture medium, time of incubation, and temperature, with that we have all along pursued, in order that our results may be strictly comparable with each other at all times of the year. The filtered waters from the general wells at the Works had an average of 41 microbes per cubic centimetre, the unfiltered water containing 9236 per cubic centimetre.

The rainfall at Oxford during March has been very near the twenty-five years' mean, which is 1·59 inches. The actual fall was 1·46, showing a deficiency of only 0·13 inch.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

NOTE ON ANTHRACENE TESTING.

By H. BASSETT.

In the course of an experimental enquiry relating to the testing of commercial anthracene, in which I have been engaged for some months past, with the view of arriving at an improved process, some variations in the results obtained seemed to indicate the existence of an unknown cause of uncertainty in the now universally employed method, namely, Meister, Lucius, and Brüning's test of October, 1876.

In this test no reference is made to the purity of the chromic acid used.

An examination of samples of crystallised chromic acid from different sources gave percentages from 87 down to 71! and showed, moreover, the presence of sulphuric acid in quantities of from 8 to 18 per cent! The gradual draining which would occur in a large bottle containing, say, ten or twelve pounds of chromic acid would obviously increase the percentage of sulphuric acid in the lowest portion, which would be very different in quality from that first taken out for use.

Under these circumstances it appeared very surprising that anything like concordant results in testing should be possible, while experience has shown a fair agreement to be the rule; but in the course of experiment this difficulty was in great measure explained; still, however, leaving no doubt that the variations in the quality of the chromic acid have caused the occasional discrepancies which could not be accounted for.

A series of comparative tests was therefore made with different samples of anthracene, using pure chromic acid, with and without the addition of sulphuric acid, but otherwise under precisely similar conditions. The table following is an example of the results obtained.

	1. B quality.	2.	3.	4. A quality.
15 grms. chromic acid ..	32·44	34·75	39·93	51·15
10 ,, ,, ..	33·98	36·34	41·13	51·53
10 grms. chromic acid + 1·8 grms. sulphuric acid ..	33·26	35·05	40·36	51·06
10 grms. chromic acid + 2·8 grms. sulphuric acid ..	33·21	35·01	40·27	51·10

The points worthy of notice in the above are :—

1. That a large deficiency in the amount of chromic acid gives, as might be expected, a considerably higher percentage of anthracene.

2. That the presence of sulphuric acid appears to compensate to a great extent for the deficiency in the chromic acid, and this is doubtless the explanation of the fact before referred to as to the usually fair agreement of tests.

3. That a considerable variation in the quantity of sulphuric acid has very little influence on the results.

4. That a good A quality anthracene is only slightly affected by considerable variations in the method of testing.

This last point is confirmed by the results already obtained by my modified process, from which I anticipate good results, and which I hope to publish on the completion of experiments now in progress with a representative series of commercial samples.

36a, St. Andrew's Hill,
Queen Victoria Street, E.C.

THE CAUSE OF LUMINOSITY IN THE FLAMES OF HYDROCARBON GASES.[*]

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.

(Concluded from p. 192).

It is perfectly possible for the temperature of a flame to be so little above the point necessary to decompose the diluted acetylene that, whilst some decomposes and renders the flame faintly luminous, the larger portion burns without decomposition. A good example of this is to be found in the combustion of alcohol, the flame of which contains as much acetylene as is to be found in a good coal-gas flame, but which is practically almost non-luminous. If alcohol in a small dish be ignited, it burns with a faintly luminous flame, and if a bell-jar is placed over it some of the products of combustion mingling with the flame still further cool it and render it non-luminous; but if now a stream of oxygen be introduced under the bell-jar, the temperature of the flame is at once increased and becomes highly luminous, whilst a cold porcelain vessel held in the flame is coated with soot.

In all the experiments in which light was developed in heated tubes by the decomposition of acetylene, the glow of the carbon was red and lurid, the light emitted being of the same character and appearance as that developed by the combustion of potassium in carbon dioxide, and entirely lacking the pure white incandescence of the acetylene flame as burnt from a flat-flame burner.

This may be due to the fact that in the open flame the temperature of the carbon particles is presumably due to three sources of heat :—

A. Heat derived from the decomposition of the acetylene molecule.

B. Heat derived from the combustion of hydrogen, carbon monoxide, and some hydrocarbons in the flame.

C. Heat derived from the combustion of the carbon particles themselves.

Whilst in the tube experiments the heat of the walls of the tube and the heat of decomposition alone are acting, and it is evident that the intensity of the heat finding its way through the walls of the tube will be very different to that exercised by the walls of burning gas which enclose the luminous portion of the flame, and there can be but little doubt that the temperature of the carbon particles will vary enormously with the rate at which the acetylene decomposes, as the more quickly the action takes place the greater will be the localising action upon the heat evolved, and the higher the incandescence of the carbon particles.

That this is so seems certain from the whiteness of the flash of light emitted when the acetylene is detonated; and experiments were made in order to, if possible, gain an idea as to how much of the incandescence of the carbon particles was due to the endothermicity of the decomposing acetylene, and how much to the action of heat and combustion on the carbon particles after formation.

In order to do this a non-luminous flat flame of large size was desired, and was obtained by using coal-gas de-illuminated by slowly passing it through bromine, well washing with sodic hydrate solution and water, and then passing it through strong sulphuric acid, the gas so treated having an illuminating value of 1·2 candles for 5 cubic ft. when burnt in the London argand at such a rate as to give a 3-inch flame, whilst in a fish-tail burner it gave a non-luminous flame. This gas gave on analysis the following percentage composition :—

Carbon dioxide	0·00
Unsaturated hydrocarbons	0·00
Carbon monoxide	5·50
Saturated hydrocarbons	33·28
Hydrogen	55·25
Nitrogen	5·49
Oxygen	0·48
	100·00

So that its combustion would give practically the same temperature and flame reactions as those in an ordinary gas-flame.

A very fine platinum tube was now obtained, closed at one end, and with five minute holes bored in a line close to the sealed end; and this having been so arranged that the holes were buried in the flame just at the top of the inner zone, acetylene was then gently allowed to flow through them into the flame.

At the points where the acetylene issued into the flame, small areas of intense luminosity were produced, whilst the liberated carbon streaming up between the flame walls of the upper zone produced dull red bands of very low luminosity. It may be suggested that the carbon particles supplied in this way to the flame may have agglomerated and formed masses larger than those produced in the ordinary way; but I do not think this, as they were completely consumed, and no smoke escaped from the crown of the flame, whereas if a flat flame is interfered with in such a way as to cause the carbon particles to roll themselves together, smoking of the flame is produced.

I think the inference to be drawn from this experiment undoubtedly is that it is the heat of decomposition which gives the high incandescence and light emitting value to the carbon particles, and that the temperature of the combustion of the other flame-gases, and finally of the carbon itself, plays but a secondary part.

In considering these results, it seems remarkable that if acetylene owes its power of rendering hydrocarbon flames luminous to its high endothermic properties, that cyanogen, which is still more endothermic, should burn under all conditions that have at present been tried with a non-luminous flame.

		Heat of Formation.
Acetylene	C_2H_2	−47,770
Cyanogen	C_2N_2	−65,700

It is clear that if the rapidity of decomposition localises the heat evolved to the products of decomposition, and that this renders the liberated carbon particles incandescent, whilst the hydrogen plays at best a very subsidiary part, it ought not to matter whether it be hydrogen or nitrogen which is combined with the carbon.

Berthelot showed that cyanogen, like acetylene, could be detonated by a small charge of mercuric fulminate; but he notes that the test is not always successful, which points to the decomposition of this body requiring a

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[*] A Paper read before the Royal Society.

greater expenditure of energy to break up the molecule than is the case with acetylene, and known facts would lead us to expect that this would be the case, as although exothermic compounds become less and less stable with rise of temperature, endothermic bodies, on the other hand, become more stable, and the endothermicity of cyanogen being greater than that of acetylene, would lead one to expect that temperatures which would decompose acetylene would have no effect on cyanogen, and that, as during the combustion of cyanogen, the liberation of nitrogen would probably have a diluting and cooling action, the cyanogen would burn directly without liberating any carbon which could emit light.

In order to see if the temperature of the cyanogen flame, when burnt from an ordinary flat-flame burner, differed much from that of hydrocarbons when consumed in a flame of the same size and kind, the temperatures were experimentally determined by the same method employed, and in the same parts of the flame, as had before been done with acetylene, ethylene, and coal-gas.

Portion of the Flame.	Temperature.
Centre of inner zone ..	1377° C.
Top of inner zone.. ..	2085
Near top of outer zone..	1645

Showing that the cyanogen flame was actually hotter than the acetylene and ethylene flames, and about the same as the coal-gas flame, but that the heat was differently distributed, the inner zone being far hotter than in the other gases, whilst the maximum temperature of the flame was at the apex of the inner zone, instead of being nearer the top of the flame.

An experiment was now made to ascertain if it were possible to decompose cyanogen with luminous deposition of carbon, by passing it through a hard glass tube heated by means of the blowpipe; but at the highest temperature attainable no trace of any deposition of carbon took place, showing how far more stable cyanogen is under the influence of high temperatures than acetylene.

The structure and characteristic appearance of the cyanogen flame have been explained by Smithells (*Chem. Soc. Journ.*, 1894, p. 603) and Dent, who conclude that the inner zone of peach blossom tint is caused by the combustion of the cyanogen to carbon monoxide and nitrogen, whilst the outer blue cone is formed by the oxidation of the monoxide to dioxide, the green fringe to the outer cone being attributed to the presence of small quantities of oxides of nitrogen; and if this explanation be accepted, it is clear that we could not obtain luminosity in the portion of the flame immediately above the inner zone, as all cyanogen has been destroyed without decomposition before that point is reached. It is conceivable, however, that although no luminosity can be detected in a cyanogen flame, and although the temperature which can be obtained in a glass tube is insufficient to break up the compound with luminous separation of carbon, yet if cyanogen could be heated to a considerably higher temperature, it might be possible to decompose it in such a way as to develope luminosity.

In order to try this point a hydrogen flame was burnt from the end of an open platinum tube 9 m.m. in diameter, and a thin platinum tube 2·5 m.m. in diameter was passed up through the broad tube to the apex of the inner zone, and a slow stream of cyanogen was admitted, with the result that the flame at once became luminous, and on surrounding the hydrogen flame with an atmosphere of oxygen to increase the temperature, the luminosity was considerably increased.

This experiment at once explains the cause of the non-luminosity of the cyanogen flame, and shows that it is purely a question of temperature, and the probabilities are that, burnt in a flame which gave sufficient heat to rapidly decompose it, nearly as high an illuminating value as that of acetylene would be obtained.

I think the explanation of the apparent anomaly of the cyanogen flame having a higher temperature than the acetylene and ethylene flames, is to be found in the fact that the molecules of cyanogen are consumed without previous decomposition, so that the heat absorbed during the formation of the cyanogen is added to the heat of combustion, and raises the average temperature of the flame, whereas with acetylene the instantaneous decomposition of the molecule before combustion confines the heat evolved to the liberated products, and the average temperature of the flame is but little more than the heat of combustion.

If the luminosity of a hydrocarbon flame is principally due to the localisation, during intensely rapid decomposition, of the heat of formation in the products, the illuminating values of such hydrocarbon gases as contain two atoms of carbon in the molecule should bear a simple ratio to their heat of formation. The gaseous hydrocarbons are—

Hydrocarbon.	Composition.	Heat Formation at Constant Pressure.
Ethane	C_2H_6	+25670
Ethylene	C_2H_4	− 8000
Acetylene	C_2H_2	−47770

And although they may undergo many changes in the flame, they will all ultimately be reduced to carbon and hydrogen again before the full luminosity of the flame is developed.

When the acetylene into which these hydrocarbons is converted by heat is decomposed, the action takes place with such enormous rapidity that one would expect the heat evolved to simply divide itself amongst the liberated atoms, so that the question of specific heat at high temperatures may be omitted.

With exothermic compounds like ethane considerable heat will have to be developed by its own combustion before it is converted into the acetylene, which, by its decomposition, endows the flame with luminosity; and if we take the ethane and call its light producing energy 1, we can then obtain a ratio of such energy for the other hydrocarbons available for distribution amongst the products of decomposition:—

$$\text{Ethane} \quad .. \quad .. \quad \frac{25670}{25670} = 1$$

$$\text{Ethylene..} \quad .. \quad \frac{25670 + 8000}{25670} = 1{\cdot}31$$

$$\text{Acetylene} \quad .. \quad \frac{25670 + 47770}{25670} = 2{\cdot}86$$

These ratios must now be divided amongst the atoms liberated at the moment of decomposition from the molecule, and we thus obtain the ratio:—

$$\begin{array}{lccccc} & C_2H_6. & & C_2H_4. & & C_2H_2. \\ & \frac{1}{8} & : & \frac{1{\cdot}31}{6} & : & \frac{2{\cdot}86}{4} \\ \text{or—} & 1 & : & 1{\cdot}74 & : & 5{\cdot}72 \end{array}$$

The determination of the illuminating value of a gas becomes more and more difficult the higher its illuminating value, owing to the cooling effect of the small burners that must of necessity be used in order to ensure complete combustion. Dr. Percy Frankland (*Chem. Soc. Journ.*, xlvii., p. 237) assigned the illuminating value of thirty-five candles to ethane as the mean of four tests, which varied considerably amongst themselves, and, adopting his figure, the calculated illuminating values for the ethane, ethylene, and acetylene would be—

	Illuminating Value.	
	Calculated.	Found.
Ethane	1 × 35 = 35	35
Ethylene	1·79 × 35 = 60·9	68·5
Acetylene.. ..	5·72 × 35 = 200·2	240

figures which are far nearer the experimental ones than could have been expected, considering the crude character of the calculation and insufficient data, which leads to omitting altogether such important factors as the amount of gas consumed to bring about the requisite temperature of decomposition, the specific heat of the products, and the thermal value of the change from gaseous to solid carbon, and are of no value except as showing that a ratio does exist between heat of formation and illuminating value.

Methane is the only other gaseous hydrocarbon of which the heat of formation is known, it being +21750, and as the molecule contains only one atom of carbon, two mols. have to be taken, and on calculating the probable illuminating value by the same method as was applied to the other hydrocarbons, we should have—

$$\frac{\left.\frac{25670 + \left\{25670 - (21750 \times 2)\right\}}{25670}\right\} \times 35}{10 \times \frac{1}{8}} = 8{\cdot}4,$$

and the illuminating value, as determined by Mr. Lewis T. Wright, is 5·2; but here, again, we know by experiment that methane requires a very high temperature to bring about its conversion into acetylene and decomposition into carbon and hydrogen, and that a large portion of the gas must be burnt without decomposition to do this.

The facts which I have sought to establish in this paper are :—

1. That the luminosity of hydrocarbon flames is principally due to the localisation of the heat of formation of acetylene in the carbon and hydrogen produced by its decomposition.

2. That such localisation is produced by the rapidity of its decomposition, which varies with the temperature of the flame and the degree of dilution of the acetylene.

3. That the average temperature of the flame due to combustion would not be sufficient to produce the incandescence of the carbon particles within the flame.

In my paper on the action of heat upon ethylene, brought before the Royal Society this spring, I showed that the decomposition of ethylene into acetylene and simpler hydrocarbons was mainly due to the action of radiant heat, and was but little retarded by dilution, whilst I have shown in this paper that the acetylene so produced requires a considerable increase in temperature to bring about its decomposition when diluted, and it is possible with these data to give a fairly complete description of the actions which endow hydrocarbon flames with the power of emitting light.

When the hydrocarbon gas leaves the jet at which it is being burnt, those portions which come in contact with the air are consumed and form a wall of flame which surrounds the issuing gas. The unburnt gas in its passage through the lower heated area of the flame undergoes a number of chemical changes, brought about by the action of radiant heat emitted by the flame walls, the principal of which is the conversion of the hydrocarbons into acetylene, methane, and hydrogen. The temperature of the flame quickly rises as the distance from the jet increases, and a portion of the flame is soon reached at which the heat is sufficiently intense to decompose the acetylene with a rapidity almost akin to detonation, and the heat of its formation, localised by the rapidity of its decomposition, raises the liberated carbon particles to incandescence, this giving the principal part of the luminosity to the flame; whilst these particles, heated by the combustion of the flame gases, still continue to glow, until finally themselves consumed, this external heating and final combustion adding slightly to the light emitted.

Any unsaturated hydrocarbons which have escaped conversion into acetylene before luminosity commences, and also any methane which may be present on passing into the higher temperatures of the luminous zone, become converted there into acetylene, and at once being decomposed to carbon and hydrogen, increase the area of the light-giving portion of the flame.

My thanks are due to Mr. F. B. Grundy for the help he has given me in the work entailed by this paper.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1895.

Dr. ARMSTRONG, President, in the Chair.

(Concluded from p. 197).

*38. "*β-Ethoxynaphthalenesulphonic Acids. The Arrest of Isomeric Change at an Intermediate Stage.*" By ARTHUR LAPWORTH,

Armstrong and Amphlett have shown (*Proc. Chem. Soc.*, 1887, 147) that when a solution of β-ethoxynaphthalene in carbon bisulphide is sulphonated by means of chlorosulphonic acid, at the ordinary temperature, two sulphonic acids are formed, one of which—the minor product—was proved to be 2 : 3′-ethoxynaphthalenesulphonic acid; they expressed the opinion that the major product was probably the 2 : 1′-acid, and showed that when the original product of sulphonation was heated merely on the water-bath this acid, with the greatest ease, underwent conversion into the isomeric 2 : 3′-acid.

Subsequently Percival, in like manner (*Ibid.*, 1889, 73), obtained two corresponding acids from β-methoxynaphthalene, and showed that in this case also the one was convertible into the other by mere heating on the water-bath. He, however, made the remarkable observation that one of the products (it was presumed that there were but two) was hydrolysed with extreme facility, a behaviour not noticed in the case of the ethoxy compounds.

These observations have served to suggest experiments, which the author has undertaken, at Professor Armstrong's request, with the object of extending the knowledge of such derivatives, and also of obtaining additional information as to the course of change on continued sulphonation. It was to be supposed that this would be more readily gained than in the case of β-naphthol itself, as it is possible to prepare crystalline sulphochlorides, &c., from ethoxy- and methoxy-acids, whilst the naphtholsulphonic acids can only be characterised by means of their salts. This anticipation has been fully confirmed. In the first place, Armstrong and Amphlett's inference that the chief product from β-ethoxynaphthalene is probably the 2 : 1′-acid was confirmed by ethylating 2 : 1′-β-naphtholsulphonic acid; an ethoxy-acid was thus obtained, yielding a sulphochloride, amide, and anilide identical with those derived from the unstable acid produced on sulphonating β ethoxynaphthalene at the ordinary atmospheric temperature.

2 : 1′-β-Ethoxynaphthalenesulphonic chloride,—

$$C_{10}H_7(OEt)SO_2Cl,$$

crystallises in large, shortened, monosymmetric prisms melting at 93°; the corresponding amide crystallises in needles melting at 165°; and the anilide forms magnificent orthorhombic prisms melting at 158°.

On nitrating potassium 2 : 1′-β ethoxysulphonate, it is converted into a mononitro-sulphonic *acid*, which crystallises from nitric acid in shining needles. The sulphochloride of this nitro-acid, which may also be prepared directly from the 2 : 1′-ethoxysulphochloride, melts at 155°; the amide at 173·4°.

2 : 3′-Ethoxynaphthalenesulphochloride crystallises in remarkably well-developed needles or tables belonging to the anorthic system, melting at 107·5°; the amide forms needles melting at 183°; the anilide small prisms melting at 152—153°.

1 : 2-Bromo-β-ethoxynaphthalene, which crystallises in small plates melting at 66°, yields practically nothing but 1-bromo-2 : 3'-sulphonic acid on sulphonation by means of chlorosulphonic acid. The same acid is obtained on brominating the 2 : 3'-ethoxysulphonic acid. The potassium salt of the acid is sparingly soluble in water, and is isomorphous with the corresponding β-naphthol and β-methoxy salts. The bromosulphochloride crystallises in tables melting at 131—132°; the amide in small pyramidal crystals melting at 191°.

Potassium 2 : 3'-β-ethoxynaphthalenesulphonate is converted into a sparingly soluble mononitro-*salt* on nitration. The corresponding chloride crystallises in anorthic plates melting at 146°; the amide is especially characteristic, crystallising in beautiful glistening prisms or needles melting at 218°.

2 : 2'-Ethoxynaphthalenesulphonic acid, prepared by ethylating the acid first described by Weinberg, yields a sulphochloride crystallising in plates which are either rhombic or monoclinic; it melts at 103°. The amide crystallises in needles melting at 172°. The anilide, which is the most characteristic compound, forms monoclinic pyramids of large size, melting at 153°.

On studying the products from β-methoxynaphthalene, it was found that the acid which undergoes hydrolysis so readily is not the 2 : 1'-acid, which, when separated, proved to be stable in solution; it followed, therefore, that three acids were formed, not two, as had been previously supposed, and it was probable that one of these was the 2 : 1-acid, as the corresponding naphthol acid is known to undergo hydrolysis very readily. Subsequent observations have justified this conclusion.

The chloride from the 2 : 3'-methoxy acid forms prisms which melt at 93°; an amide, crystallising in needles, which melt at 199°; and an anilide, crystallising in silky needles, melting at 79—80°.

The sulphochloride of the 2 : 1'-methoxy acid, like the corresponding ethoxy-compound, crystallises in large monoclinic prisms, or plates, melting at 137°; the amide crystallising in needles which melt at 153°, and the anilide crystallising in anorthic tables melting at 196°.

When the chlorides of these acids are heated or distilled, either alone or with phosphorus pentachloride, they do not yield the corresponding chloro-derivatives of naphthol, but either suffer complete decomposition or undergo chlorination.

On disulphonating ethoxynaphthalene at the atmospheric temperature, a very mixed product was obtained, from which it was found possible to isolate the disulphonic acids only after the expenditure of much time and labour. A surprising amount of 2·3'-salt accompanied the 2·1'-sulpho salt.

Only one disulphonic acid is formed in any appreciable quantity; this gives salts which, on the whole, are badly characterised, but yields a chloride of a well-defined character. This crystallises from benzene in large transparent monoclinic crystals which contain $1\frac{1}{3}$ mol. of benzene of crystallisation, and melt when heated quickly at 51°. The chloride itself forms ill-defined plates melting at 10° C.; the amide crystallises in needles melting at 253—254°, the anilide anorthic plates melting at 127°.

In order to determine the nature of this disulphonic acid, solutions of the 2·1' and 2·3'-sulphonic chloride in warm chloroform were separately sulphonated with SO_3HCl, a novel method which has been found to afford most satisfactory results; on adding water to the products the sulphonated sulphochlorides at once dissolve, hydrolysis occurring immediately.

The 2·1'-sulphochloride yields an acid which was found to be identical with that produced on ethylating 2 : 1' : 3'-β-naphtholdisulphonic acid. Both products gave a sulphochloride crystallising in monoclinic prisms melting at 158° and the same amide and anilide.

The disulphonic acid from the 2·3'-disulphochloride on the other hand was found to be identical with the acid formed directly from ethoxynaphthalene, and as it was different from the 2 : 1' : 3'-disulphochloride the conclusion was arrived at that the constitution was EtO:S:S = 2 : 1 : 3'. If such be the case, it follows that the first product of sulphonation of ethoxynaphthalene must be the 2-1-acid.

This result therefore led the author to sulphonate ethoxynaphthalene at as low temperature as possible by adding the chlorosulphonic acid to a solution cooled by a weak freezing mixture; the product was found to consist practically entirely of the 2 : 1-acid. On allowing the product to stand, however, merely at the ordinary temperature, during only about twelve hours, it was found that it underwent change chiefly into the isomeric 2 : 1'-acid, a small proportion of the 2 : 3'-acid being also formed. As the 2 : 1-acid is very easily hydrolysed, the separation of methoxynaphthalene observed by Percival is easily accounted for.

Judging from the manner in which the 2 : 1'-acid is thus formed, it is difficult to avoid the conclusion that its production from the 2 : 1-acid is due to direct isomeric change; and if it be supposed that the production of the 2 : 3'-acid is due to further isomeric change, this would appear to be the first case in which the arrest of isomeric change at an intermediate stage has been observed.

2 : 1-Ethoxynaphthalenesulphonic chloride crystallises in long needles melting at 115—116°, its amide forms monoclinic prisms melting at 158°, and the anilide is also monoclinic, crystallising in large pyramids melting at 187°. The sulphonic group is at once displaced by the action of either nitric acid or bromine.

2 : 3 : 3'-Ethoxynaphthalenedisulphonic acid, prepared by ethylating the corresponding naphthol acid, yields a chloride crystallising in ill-defined plates melting at 121°.

It is proposed to complete the series of ethoxysulphonic acids. The behaviour of α-ethoxynaphthalene will form the subject of a later communication.

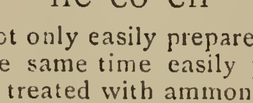
Discussion.

The President said that it was very noteworthy that Dr. Moody had failed to corroborate the statements of all previous workers with ortho- and metaxylene, ethylbenzene, and methoxy- and ethoxybenzene, finding that none of these gave isomeric acids on sulphonation: having taken the very greatest pains to purify the materials he had used, he had not been misled by impurities. The readiness with which the ortho acids in all cases underwent change was remarkable, but most remarkable of all was the difference which he had established between methylbenzene (toluene) and ethylbenzene. The non-appearance of ortho-acid when the latter was sulphonated was probably to be accounted for by the extreme readiness with which the ortho-acid, conceivably the initial product of sulphonation, underwent "isomeric change," but whatever the explanation, the observation of so striking a difference in the behaviour of homologous methyl and ethyl derivatives was of great interest.

Mr. Lapworth's discovery that it was possible to arrest "isomeric change" at an intermediate stage was a very remarkable one; such results were of extreme importance as furnishing the materials required for the discussion of the mechanism of isomeric change.

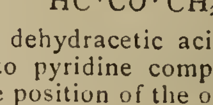
39. "*Some Oxypyridine Derivatives.*" By Miss A. P. Sedgwick and N. Collie, Ph.D.

The authors have made a number of pyridine compounds from the derivatives of dehydracetic acid. The original object of the research was to produce as many oxypyridine derivatives as possible, whose constitutional formulæ would be known. Two substances, dimethyl pyrone and the lactone of triacetic acid,—



$$\begin{array}{l} CH_3{\cdot}C{-}O{-}C{\cdot}CH_3 \\ \quad \| \qquad\quad \| \\ \quad HC{\cdot}CO{\cdot}CH \end{array}$$

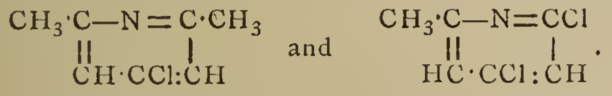
and



$$\begin{array}{l} CH_3{\cdot}C{-}O{-}CO \\ \quad \| \qquad\quad | \\ \quad HC{\cdot}CO{\cdot}CH_2 \end{array},$$

are not only easily prepared from dehydracetic acid, but at the same time easily pass into pyridine compounds when treated with ammonia. The position of the oxygen atoms in the pyridine ring is also known. Oxy-pyridines are substances which possess all the marked and characteristic properties of phenols and quinones, but up to the present we are only acquainted with a very few of these compounds.

The pyridine derivatives, used by the authors as a starting-point in the research, were *γ-chloro-αα′-dimethyl pyridine, and αγ-dichloro-α′-methyl pyridine*,—



$$\begin{array}{ccc} CH_3\cdot C—N=C\cdot CH_3 & & CH_3\cdot C—N=CCl \\ \| \quad\quad\quad | & \text{and} & \| \quad\quad\quad | \\ CH\cdot CCl:CH & & HC\cdot CCl:CH \end{array} .$$

By the action of dilute permanganate of potash on the first of these, two acids were obtained. The first, *γ-chloro-αα′-pyridine dicarboxylic acid*, is sparingly soluble in water, but crystallises well from acetic acid with 1 mol. of water of crystallisation; when heated it chars at about 220° without melting. A very characteristic reaction of this substance is the production of a brilliant cherry-red colouration with ferrous sulphate.

γ-Oxy-αα′ pyridinedicarboxylic Acid or Chelidamic Acid.—This substance was produced from the foregoing acid by careful fusion with potash. It possessed all the properties of chelidamic acid, prepared from chelidonic acid; when it is heated to 260°, carbon dioxide is copiously evolved, *γ-oxypyridine*, m. p. 66°, being formed.

α-Methyl-γ chloro-α′-pyridinecarboxylic Acid.—This is the second acid which is produced when γ-chlorolutidine is oxidised with potassium permanganate: it is more soluble in water than the first acid. Its m. p. is 93°; it crystallises in long needles without water of crystallisation. When strongly heated it decomposes, yielding *γ-chloro-picoline*. This compound is a liquid, b. p. 162·5—163·5°. It is possibly the same as a chloropicoline noticed by Ost (*Ber.*, xvi., *Ref.*, 1374), which he obtained by reducing pentachloropicoline with tin and hydrochloric acid. When γ-chloropicoline is oxidised with permanganate of potash it is converted into *γ-chloropicolinic acid*, m. p. 194—195°, and this acid when fused with potash yields *γ-oxypicolinic acid*, which melts at 263—264°. When the lactone of triacetic acid is heated with ammonia dioxypicoline is formed; the compound can be quantitatively converted into *αγ-dichloro-α′-methyl pyridine*. This chloride on oxidation with permanganate is converted into *αγ-dichloropicolinic acid*, m. p. 101—102°, which crystallises in long needles. When heated it does not yield dichloro-pyridine, but suffers complete decomposition. If it is boiled with sodium ethylate it is completely converted into *αγ-ethoxypicolinic acid*, which melts at 93—95°, and this substance yields *αγ-dioxypicolinic acid* when boiled with fuming hydriodic acid. This oxy-acid melts at 270—273°, and is isomeric, though not identical with, another dioxypicolinic acid, comenamenic acid. Several attempts were made to prepare αγ-dioxypyridine, but without success. *αγ-Diethoxypicoline* was made from dichloropicoline by boiling it with sodium ethylate. It is a sweet smelling oil, which boils between 238—240°.

40. "*On the Colouring Principle of* '*Toddalia aculeata*' *and* '*Evodia meliæfolia*.'"

By A. G. Perkin and J. J. Hummel.

Toddalia aculcata is an Indian plant belonging to the Rutaceæ. Its root bark is used in Madras as a yellow dye-stuff; it also possesses valuable medicinal qualities. The authors find that the colouring matter is berberine, contrary to the statement of Flückiger and Hanbury, who were unable to detect this alkaloid.

Evodia meliæfolia, belonging to the same natural order, is a tree growing in China and Japan, whose bark is largely employed in medicine and in dyeing. The authors confirm previous statements that the bark contains berberine.

Comparative dyeing experiments on wool indicated that Evodia and Toddalia bark possess the same tinctorial power as a 3 per cent solution of berberine hydrochloride.

41. "*Some Ethereal Derivatives of Sarcolactic Acid.*"

By Percy Frankland, Ph.D., B.Sc., F.R.S., and James Henderson, B.Sc.

The authors have prepared sarcolactic acid in quantity by the fermentation method previously described by Percy Frankland and MacGregor (*Trans.*, 1893, 1028). Of this sarcolactic acid they have prepared the following derivatives: methylic and ethylic sarcolactate, methylic and ethylic acetylsarcolactate, ethylic benzoylsarcolactate.

The optical and other constants determined are given in the accompanying table.

The relationship between these and the corresponding derivatives of active glyceric acid is discussed. The more important points are:—

1. The small effect on the rotation of substituting ethyl for methyl in the lactate compared with that in the glycerate.
2. The much greater increase in the rotation effected by acetylating the lactate than by diacetylating the glycerate.
3. The reversal of the sign of rotation by the introduction of the benzoyl group. This is also the effect of introducing two benzoyl groups into the glycerates.
4. The comparatively slight difference in rotation exhibited by the methylic and ethylic lactates probably points to the latter exhibiting the "maximum" in this series of ethereal salts; the maximum, as calculated from the product of asymmetry, should be exhibited by the methylic salt; in the glyceric series the calculated maximum is exhibited by the propyl, and actually by the tributyl compound. The coincidence in both cases is, therefore, probably similar.
5. The ethereal salts of glyceric acid exhibit a diminishing density in ascending the series from the methylic to butylic; the diacetylglycerates have lower densities than the corresponding glycerates, excepting in the case of the heptyl and octyl compounds, of which the diacetyl glycerates have a greater density than the corresponding glycerates, or, in other words, the density curves of the glycerates and diacetylglycerates cross at the maximum (the butyl compound). The same phenomenon is repeated in the case of the lactates; methylic acetyl-lactate has a lower density than methylic lactate; ethylic acetyl-lactate has a higher density than ethylic lactate.
6. This intersection of the density curve is also in both cases attended with a remarkable change in the optical relationship, which may be stated thus: the greater the diminution in the density effected by acetylating, the greater is the increase in the rotation produced by this constitutional change; and when the effect of acetylating is to increase the density, the increment in rotation is

Ethereal salts.	Boiling-point (uncorr.).	Relative density, 15°/15°.	Observed rotation at 15° C., α_D. (198·4 m.m. tube).	Specific rotation, $[\alpha]_D$.	Molecular rotation, $\frac{M[\alpha]_D}{100}$	Molecular deviation, $[\delta]_D = \frac{\alpha}{L}\sqrt[3]{\frac{M}{d}}$.	Product of asymmetry ($P \times 10^6$).
	°	°	°	°	°	°	°
Methylic sarcolactate ..	143—145	1·1017	−15·00	−6·86	−7·13	−34·4	79·16
Ethylic sarcolactate	152—154	1·0414	−17·90 (at 16·5° C.)	−8·66	−10·22	−43·7	73·84
Methylic acetylsarcolactate	170—171·5	1·0957	−94·36	−43·41	−63·38	−242·9	0
Ethylic acetylsarcolactate	179·5—180·5	1·0327	−86·62	−41·47	−66·35	−232·9	198·6
Ethylic benzoylsarcolactate	154—155·5 (15 m.m.)	1·1164 (14·9°/14·9°)	+49·2	+22·22	+49·33	+144·7	416·2

markedly less than in those cases in which the density is diminished by the process. This applies also to both glycerates and lactates.

7. The effect of benzoylating is to increase the density, whilst at the same time it enormously diminishes the rotation, as well as reversing the sign of the latter. This again holds good for both glycerates and lactates.

42. "*Electrolysis of Potassium Allo-ethylic Camphorate.*" By James Walker, D.Sc., and James Henderson, B.Sc.

The chief products obtained on electrolysing potassium allo-ethylic camphorate are the ethylic salts of an unsaturated acid, $C_9H_{14}O_2$, and of a dibasic saturated acid, $C_{18}H_{30}O_4$. These acids have been named *allo-campholytic* and *allo-camphothetic* acids respectively. The former acid gives a liquid dibromide, and can be converted into the isomeric campholactate of Fittig and Woringer. It is not identical with lauronolic acid, which also yields campholactone on similar treatment. The isolauronolic acid of Kœnigs and Hœrlin is identical with isocampholytic acid. The results obtained indicate that camphoric acid contains the group $\cdot\dot{C}H\cdot CH(COOH)\cdot\dot{C}(COOH)$.

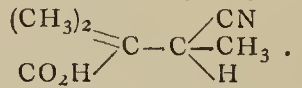
43. "*Trimethylsuccinic Acid.*" By W. A. Bone, M.Sc., Ph.D., and W. H. Perkin, jun., Ph.D., F.R.S.

For some time the authors have been working with this acid and the isomeric dimethylglutaric acids, and, although their experiments are not yet complete, the recent appearance of a paper by Auwers on the same subject (*Ber.*, xxviii., 263) renders the publication of this short notice necessary.

There has been a good deal of discussion as to whether trimethylsuccinic acid exists in one or two modifications. The authors have prepared this acid by two different methods, viz. (1) by the action of ethylic α-bromisobutyrate on the sodium derivative of ethylic α-cyanopropionate (Zelinsky, *Ber.*, xxiv., 468); (2) and by the action of ethylic α-bromisobutyrate on the sodium derivative of ethylic methylmalonate dissolved in xylene at 180° (Bischoff, *Ber.*, xxiv., 1041). The products were in each case hydrolysed, and the acid heated at 200°. The authors find that one and the same trimethylsuccinic acid is always formed, and that when pure this melts at 152°; and they are able to confirm the results recently obtained by Auwers, which differ materially from those described by Zelinsky (*Ibid.*), Bischoff (*Ibid.*), and Hell ("Inaug. Diss.," Bonn, 1893).

Trimethylsuccinic acid is characterised by yielding a very insoluble calcium salt, which affords a convenient method for separating it from the isomeric dimethylglutaric acids, which are always formed in the above interactions. When heated with acetic anhydride, trimethylsuccinic acid yields an anhydride melting at 38—39°.

During the course of their experiments, the authors have also obtained cyanotrimethylpropionic acid,—



$$\begin{matrix}(CH_3)_2 \\ CO_2H\end{matrix}\!\!>\!C-C\!\!\begin{matrix}\diagup CN \\ -CH_3 \\ \diagdown H\end{matrix}\ .$$

This acid crystallises in colourless needles, melting at 126°, and it is characterised by yielding a sparingly soluble ammonium salt, which crystallises from water in long colourless needles. Acetic anhydride converts cyanotrimethylpropionic acid into a crystalline substance melting at 65°, which is at present under investigation. On hydrolysis with concentrated hydrochloric acid, cyanotrimethylpropionic acid yields trimethylsuccinic acid, which shows that it must have the constitution represented above.

A description of the results recently obtained in the investigation of the isomeric symmetrical dimethylglutaric acid, which is not yet concluded, is reserved for a future paper.

44. "*New Isomeric Sulphonic Chlorides derived from Camphor.*" By F. Stanley Kipping, Ph.D., D.Sc., and William J. Pope.

In our first paper on the sulphonic derivatives of camphor (*Trans.*, 1893, lxiii., 548) the separation of dextrorotatory camphor sulphonic chloride and of the corresponding optically inactive compound was described, and it was mentioned that the crude oily product obtained by the interaction of sodium camphorsulphonate and phosphorus pentochloride contained other crystalline compounds of unknown composition. As it seemed possible that these by-products might prove to be interesting derivatives of camphor, their investigation has been continued; two new crystalline substances have now been isolated from the mixture.

The compounds in question are isomeric sulphonic chlorides of the composition $C_{10}H_{14}Cl\cdot SO_2Cl$, and both are optically inactive; we propose for the present to call them *chlorocamphenesulphonic chlorides*, at any rate until further study shows that they are not, as we believe them to be, camphene derivatives.

α-Chlorocamphenesulphonic chloride may be obtained in beautiful, massive, transparent crystals, but it is much more readily soluble than either of the camphorsulphonic chlorides in all ordinary solvents, and dissolves freely even in boiling light petroleum (b. p. 40—50°); it melts not quite sharply, at 83—84°, and appears to be dimorphous, as, when the liquefied substance is rapidly cooled, it solidifies to an opaque mass which does not melt until 86—87°.

α-Chlorocamphenesulphonamide, $C_{10}H_{14}Cl\cdot SO_2\cdot NH_2$, is obtained on shaking the sulphonic chloride with cold concentrated ammonia; it crystallises from dilute alcohol in transparent plates melting at 161—162°, and is only sparingly soluble in water.

α-Dichloracamphene, $C_{10}H_{14}Cl_2$, is formed in large quantities when α-chlorocamphenesulphonic chloride is heated for a short time at 160—170°; it crystallises from dilute alcohol in fern-like forms melting at 72—73°, and is readily volatile in steam.

β-Chlorocamphenesulphonic chloride appears to be present in the crude oily product in much smaller quantities than the corresponding α-compound, and, being much more readily soluble than the latter, it is isolated only with difficulty; it dissolves freely even in cold light petroleum (b. p. 30—40°) from which it crystallises in large, transparent plates which become opaque when heated gently in contact with the mother-liquor; its melting-point is 77—78°.

β-Chlorocamphenesulphonamide, $C_{10}H_{14}Cl\cdot SO_2\cdot NH_2$, crystallises from dilute alcohol in plates, and melts at 156—157°.

When the β-sulphonic chloride is heated at about 160° it is rapidly decomposed, sulphur dioxide being evolved; the main product is a colourless, very volatile, pleasant-smelling oil, but a small quantity of a crystalline substance is also obtained.

In their behaviour, when heated, these two chlorocamphenesulphonic chlorides evidently resemble the sulphonic derivatives of camphor, which, as we have recently shown, are readily converted into halogen derivatives, losing sulphur dioxide. The exact manner in which these two by-products are formed is not yet known, but it seems probable that they are produced by the action of phosphorus pentachloride on camphorsulphonic chloride.

NOTICES OF BOOKS.

The Progress of Science: its Origin, Course, Promoters, and Results. By J. Villin Marmery. With an Introduction by Samuel Laing. 8vo. London: Chapman and Hall. 1895.

In this painstaking and accurate work the Author has given us an account of the rise and development of Science from the earliest times up to the present day.

It will be obvious to all that, in dealing with so stupendous a subject within the limits of some 400 pages, this work *must* of necessity treat briefly of many important and interesting facts. On the other hand,—and that, in our opinion, greatly enhances the value of the work,—there is a copious and well-arranged Bibliography, which indicates to the Student, at a glance, where he may further pursue the study of the questions here introduced to his notice.

In these days, when we are under the thrall of "Examinationism," it is refreshing to find a book of this character which has not been compiled in accordance with any required Syllabus to meet the needs of a particular examination, but launches out on an independent track boldly and fearlessly, and at the same time honestly and straightforwardly.

The chapter which is devoted to the Progress of Science among the Arabs is one of the attractions of the book. It is pointed out that, up to now, sufficient justice has not been done to the Arabs.

Another very interesting feature is the chapter devoted to the vindication of Roger Bacon, in which the author contends that Roger Bacon was vastly the superior of Francis Bacon, and preceded the latter in the subject-matter which makes up the "Novum Organum."

Turning to the chapter on Modern Science, we find that the author has treated this difficult subject with care and judgment. Especially may we refer to the sections devoted to the weighing of the relative claims of Priestley and Lavoisier, and to the consideration of Crookes's speculation on the Genesis of the Elements.

The Index is copious and excellent.

We cordially wish the author every success in his bold venture, and we trust that the work may meet with the circulation which its merits deserve.

Essays of Jean Rey, Doctor of Medicine. On an Enquiry into the Cause wherefore Tin and Lead Increase in Weight on Calcination (1630). Crown 8vo., pp. 54. Edinburgh: W. F. Clay. London: Simpkin, Marshall, Hamilton, Kent, and Co. (Ltd.). 1895.

This little work forms No. 11 of the series of the "Alembic Club Reprints." It is an interesting step towards the right understanding of the process of oxidation as established by Lavoisier a century and a half later. The author still recognises the four elements of antiquity, earth, water, air, and fire, though he contends that all matter possesses weight. At times there crops up a mention of the three chemical elements, salt, sulphur, and mercury. He shows himself versed in the principles of experimental enquiry. But he holds that water is "a simple substance beyond question." By a series of experiments he demonstrates that "it is not the disappearance of the celestial heat giving life to the lead, or the death of the latter, which augments its weight on calcination,"—a highly metaphysical, or rather unphysical, notion,—that it is not the consumption of the aërated particles which augments the weight of the lead, that the increase does not come from the vessel, that it is not due to the vapours from the charcoal, or the "volatile salt of the charcoal," or the mercurial volatile salt, or the moisture attracted by the calx; and he asks why it does not increase in weight infinitely? But he does not raise the converse question, why a given volume of air does not increase the weight of an unlimited quantity of lead or tin? Had he done this experimentally he would have trodden very closely upon the heels of Lavoisier and Priestley; but he regards air as a simple substance, saving the presence of certain possible impurities.

The perusal of this book will show us what an amount of erroneous and obscure notions had to be got rid of before the rational progress of chemistry could commence.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 14, April 8, 1895.

On the Fluted Spectrum.—H. Poincaré.—This memoir is too exclusively mathematical for transference to our pages.

Transfer of the Capital of Brazil.—H. Faye.—This startling enterprise seems to be dictated by sanitary considerations. The new capital will be placed at an altitude of 1000 metres. The climate is said to resemble that of the extreme south of France. The water supply will exceed 1000 litres per head for a population of a million, and there will be no danger of malaria.

A New Apparatus called the Comparative Hema-Spectroscope.—M. de Thierry.—This apparatus, extremely sensitive, offers every guarantee of exactitude, and may render services in forensic medicine, in biological and analytical chemistry, and in physics by the comparative study of the absorption spectra of liquids examined in a great thickness. Its construction cannot be described intelligibly without the accompanying figure.

Simple Experiment showing the Presence of Argon in Atmospheric Nitrogen.—M. Guntz.—As an absorbent for argon the author has selected lithium, which combines readily with nitrogen at a temperature below dark redness. After the introduction of a sufficient volume of atmospheric nitrogen the apparatus remains full of argon. If, on the contrary, nitrogen is introduced from the decomposition of a chemical compound nothing remains unabsorbed.

The Spectra of Selenium and of some Native Selenides.—A. de Gramont.—The author gives an elaborate table of the rays in the spectrum of selenium and of Berzeline, Cu_2Se, Zorgite, $(PbCu_2)Se$, Claisthalite, $PbSe$, Eucainite, Cu_2Se,Ag_2Se (from Atacama), and Guarajuatite, Bi_2Se_3.

Determination of Thiophene in Benzene.—G. Denigès.—The author places in a 60 grm. flask 20 c.c. of his mercuric reagent, HgO 50 grms., SO_4H_2 200 c.c., water 1 litre, and adds 2 c.c. of benzene. He stoppers the flask, keeps the cork in its position by means of a wire, and heats in a boiling water-bath for a quarter of an hour, agitating frequently so as to emulsify the benzene with the reagent. At the end of this time it is allowed to cool and filtered through a tared filter, washed with boiling water, and dried at 110°—115° until the weight is constant, and weighed. The increase of the weight of the filter multiplied by $\frac{84}{1108} = 0{\cdot}0758$ shows the quantity of thiophene contained in the 2 c.c. of benzene.

Action of Potassium Permanganate with various Organic Matters.—E. Maumené.—The author states that manganese peroxide has always been regarded as insoluble in water, in the majority of dilute acids, and especially in neutral media, sugar, alcohol, &c. As far as sugar is concerned this is an error.

On the Calcium Phosphate of Milk.—L. Vaudin.—The author concludes from his experiments that—1. Milk contains citric acid in the state of an alkaline citrate, which contributes to keep in solution the calcium phosphate present. 2. This solution is due to the important part played by lactose in presence of alkaline citrates. 3 All circumstances which may modify or destroy the molecular equilibrium of the salts dissolved in the milk tend to precipitate tricalcic phosphate with an excess of lime in the state of citrate.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 107.

This number contains no chemical matter.

Archives Néerlandaises des Sciences Exactes et Naturelles. Vol. xxviii., Part 5.

This issue contains no chemical matter.

MISCELLANEOUS.

Zeitschrift für Anorganische Chemie.—We are happy to announce that this valuable journal will not be suspended in consequence of the regretted death of Dr. G. Krüss, its late editor. It will be continued by Dr. Richard Lorenz, a "privat docent" of the University of Göttingen, with the co-operation of Professor W. Nernst, and will be published as before by the firm of Leopold Voss, of Hamburg. The editor, whilst retaining the characters of the *Zeitschrift*, purposes to include in addition chemical physics and electro-chemistry. It has our best wishes for its continued success.

MEETINGS FOR THE WEEK.

MONDAY, 29th.—Society of Arts, 8. (Cantor Lectures). "Recent American Methods and Appliances employed in the Metallurgy of Copper, Lead, Gold, and Silver," by James Douglas.
TUESDAY, 30th.—Royal Institution, 3. "Alternating and Interrupted Electric Currents," by Professor George Forbes, F.R.S.
— Institute of Civil Engineers, 8.
WEDNESDAY, May 1st.—Society of Arts, 8. "Deviations of the Compass," by Prof. A. W. Reinold, F.R.S.
— Royal Institution, 5. (Annual Meeting).
THURSDAY, 2nd.—Royal, 4 30.
— Royal Institution, 3. "The Liquefaction of Gases," by Prof. Dewar, F.R.S.
— Chemical, 8.
FRIDAY, 3rd.—Royal Institution, 9. "The Structure and Function of the Horse's Foot," by Veterinary Captain Frederick Smith.
— Quekett Club, 8.
— Geologists' Association, 8.
SATURDAY, 4th.—Royal Institution, 3. "English Music and Musical Instruments of the 16th, 17th, and 18th Centuries," by Arnold Dolmetsch.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1849.

ON A
GAS SHOWING THE SPECTRUM OF HELIUM, THE REPUTED CAUSE OF D_3, ONE OF THE LINES IN THE CORONAL SPECTRUM.[*]

By WILLIAM RAMSAY, F.R.S.,
Professor of Chemistry, University College, London.

In the course of investigations on argon, some clue was sought for which would lead to the selection of one out of the almost innumerable compounds with which chemists are acquainted, with which to attempt to induce argon to combine. A paper by W. F. Hillebrand, "On the Occurrence of Nitrogen in Uraninite, &c." (*Bull. of the U. S. Geological Survey*, No. 78, p. 43), to which Mr. Miers kindly directed my attention, gave the desired clue. In spite of Hillebrand's positive proof that the gas he obtained by boiling various samples of uraninite with weak sulphuric acid was nitrogen (p. 55)—such as formation of ammonia on sparking with hydrogen, analysis of the platinochloride, vacuum-tube spectrum, &c.—I was sceptical enough to doubt that any compound of nitrogen, when boiled with acid, would yield free nitrogen. The result has justified the scepticism.

The mineral employed was clèveite, essentially a uranate of lead, containing rare earths. On boiling with weak sulphuric acid a considerable quantity of gas was evolved. It was sparked with oxygen over soda, so as to free it from nitrogen and all known gaseous bodies except argon; there was but little contraction; the nitrogen removed may well have been introduced from air during this preliminary experiment. The gas was transferred over mercury, and the oxygen absorbed by potassium pyrogallate; the gas was removed, washed with a trace of boiled water, and dried by admitting a little sulphuric acid into the tube containing it, which stood over mercury. The total amount was some 20 c.c.

Several vacuum-tubes were filled with this gas, and the spectrum was examined, the spectrum of argon being thrown simultaneously into the spectroscope. It was at once evident that a new gas was present along with argon.

Fortunately, the argon-tube was one which had been made to try whether magnesium-poles would free the argon from all traces of nitrogen. This it did; but hydrogen was evolved from the magnesium, so that its spectrum was distinctly visible. Moreover, magnesium usually contains sodium, and the D line was also visible, though faintly, in the argon-tube. The gas from clèveite also showed hydrogen lines dimly, probably through not having been filled with completely dried gas.

On comparing the two spectra, I noticed at once that while the hydrogen and argon lines in both tubes accurately coincided, a brilliant line in the yellow, in the clèveite gas, was nearly *but not quite* coincident with the sodium line D of the argon-tube.

Mr. Crookes was so kind as to measure the wave-length of this remarkably brilliant yellow line. It is 587·49 millionths of a millimetre, and is exactly coincident with the line D_3 in the solar chromosphere, attributed to the solar element which has been named *helium*.

Mr. Crookes has kindly consented to make accurate measurements of the position of the lines in this spectrum, which he will publish, and I have placed at his disposal tubes containing the gas. I shall therefore here give only a general account of the appearance of the spectrum.

While the light emittted from a Plücker's tube charged with argon is bright crimson, when a strong current is passed through it, the light from the helium-tube is brilliant golden-yellow. With a feeble current the argon-tube shows a blue-violet light, the helium-tube a steely-blue, and the yellow line is barely visible in the spectroscope. It appears to require a high temperature, therefore, to cause it to appear with full brilliancy, and it

	Argon-tube.	*Helium-tube.*	
Red	1st triplet.	1st triplet.	Equal in intensity.
	2nd pair.	2nd pair.	,, ,,
	Faint line.	Faint line.	,, ,,
	Stronger line.	Stronger line.	,, ,,
	Brilliant line.	Dull line.	Weak in helium.
	Strong line.	Very dim line.	
Red-orange	Moderate line.	Moderate line.	Equal in intensity.
	,, ,,	,, ,,	,, ,,
	,, ,,	,, ,,	,, ,,
Orange	Faint line.	Faint line.	,, ,,
	Triplet.	Triplet.	,, ,,
Orange yellow	Pair.	Pair.	,, ,,
Yellow	Absent.	Brilliant.	W = 587·49. (the helium line, D_3).
Green	7 lines.	7 lines.	Equal in intensity.
Green-blue	5 lines.	5 lines.	,, ,,
	Absent.	Faint.	In helium only.
	Absent.	Brilliant.	,, ,,
Blue	Absent.	8 lines.	,, ,,
Blue-violet	3 lines, strong.	Barely visible, if indeed present at all.	
	2, fairly strong.	2, fairly strong.	Equal in intensity.
Violet	Absent.	Bright line.	In helium only.
	Absent.	4 bright lines.	
	Violet pair.	Violet pair.	Equal in intensity.
	Single line.	Single line.	,, ,,
	Triplet.	Triplet.	,, ,,
	Triplet.	Triplet.	,, ,,
	Pair.	Pair.	,, ,,

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[*] A Paper read before the Royal Society, April 25th, 1895.

may be supposed to be part of the high-temperature spectrum of helium.

The accompanying table gives a qualitative comparison of the spectra in the argon-* and in the helium-tubes.

It is to be noticed that argon is present in the helium tube, and by the use of two coils the spectra could be made of equal intensity. But there are sixteen easily visible lines present in the helium-tube only, of which one is the magnificent yellow, *and there are two red lines strong in argon and three violet lines strong in argon, but barely visible and doubtful in the helium-tube.* This would imply that atmospheric argon contains a gas absent from the argon in the helium-tube. It may be that this gas is the cause of the high density of argon, which would place its atomic weight higher than that of potassium.

It is idle to speculate on the properties of helium at such an early stage in the investigation; but I am now preparing fairly large quantities of the mixture, and hope to be able before long to give data respecting the density of the mixture, and to attempt the separation of argon from helium.

ON THE
PRESENCE OF HELIUM IN CLÈVEITE.

By P. T. CLÈVE.

We have examined the gas of clèveite at the laboratory of the University of Upsala, and I judge it proper to communicate to you the result.

The mineral had been found at Carlshaus, in Norway. One of my pupils, Herr Langlet, heated a mixture of the mineral with potassium disulphate in a combustion tube. The gas, after being passed over copper at redness, was collected over a concentrated solution of potassa.

The spectrum of the gas does not display the lines of argon, as we have been able to verify by means of a tube argon which I have received from Prof. Ramsay. According to the measurements of Prof. Thalén, the rays are:—

Wave-lengths.	Atlas.	Intensities.
λ 6677	Angström.	Medium strong.
λ 5875·9	Micrometric measurement.	Strong.
λ 5048	Rowland Photog. charts.	Medium strong.
λ 5016		Strong.
λ 4922		Medium strong.
λ 4713·5	Angström.	Weaker.

The presence of helium in a terrestrial substance is therefore established. It appears probable that the strong helium line (λ 5875·9) is accompanied on each side by two very faint lines.—*Comptes Rendus*, cxx., p. 834.

OBSERVATIONS ON ARGON: FLUORESCENT SPECTRUM.

By M. BERTHELOT.

Prof. Ramsay, since his recent visit to Paris, has had the kindness to send me a second specimen of argon, amounting to 90 c.c., to subject it to further experiments. Before describing them I consider it my duty to thank him, and to invoke his guarantee for the purity of the specimens of a gas which I have not myself prepared.

These fresh experiments have referred principally to the study of the fluorescence spectrum which is observed with argon charged with vapour of benzene, and submitted to the moderate action of the effluve on certain conditions which seem to correspond to a particular state of equilibrium; for the quantity of gas absorbed does not exceed some hundredths, even after a considerable time. This limited equilibrium is analogous to that of the combination of nitrogen and hydrogen under similar circumstances.

For this purpose an observation is necessary. In fact, the two specimens of gas which have been sent me successively behaved in a slightly different manner, though giving equally signs of combination in presence of benzene. With the second the absorption was found limited to between six- and ten-hundredths of the original volume, whilst the first specimen has undergone successive absorptions which reduced it to the fifth of its original volume. This difference may correspond to particular conditions which I have not yet succeeded in defining, as I now do, for the production of fluorescence; but it may also be explained by the existence in the first specimen of a considerable proportion of nitrogen introduced by some accident in filling and sealing the tube which was sent me. To this question I purpose returning.

However it may be, these are the conditions of the fluorescence excited by the effluve:—

I operated with the assistance of a powerful Ruhmkorff's coil, fitted with a Leyden jar and a Marcel Deprez interrupter actuated by a battery or by accumulators; the length of the sparks which could be occasioned between the external wires being from 10 to 12 m.m. In several experiments I found it advantageous to interrupt one of these wires, so as to determine a flow of sparks in front of the tube submitted to the effluve; we succeed even with a sensibly greater external striking distance.

We will first explain the phenomenon in a general manner before giving measurements relating to the rays observed.

Under the above condition, at the end of a time varying from fifteen minutes to four or five hours, the silent discharges became gradually luminous, and the tube was lighted up, in almost its entire extent, at first with a violet tint with a reddish rain of fire; then the fluorescence took a lustre more and more intense, and changed gradually to a splendid green shade, visible at a distance even in full daylight, but more brilliant in darkness. With a greater striking distance the light became blue.

At this point the phenomenon remained for several hours. On stopping the current the light was at once extinguished. On re-establishing it, it at once reappeared if the stoppage had been of a brief duration; at the end of some minutes, if it had been longer the light reappeared, setting out from the point where the electric tension is greatest. Still after the lapse of a certain number of hours, especially if we increase the intensity of the discharges, the green tint is finally extinguished, leaving only a milky light which cannot be analysed by the spectroscope. All these phenomena have been reproduced from eight to ten times in different tubes; they are manifested in the gas near the atmospheric pressure, which is very characteristic.

On directing an ordinary spectroscope to the fluorescent tube we see appear a series of rays very distinct and specific,—that is to say, a yellow ray, a green ray (the most brilliant of all), and two violet rays less visible, especially the last, which is not well seen except in darkness. We see also certain rays or bands in the violet region, in the green, and especially in the red and the orange region, but I have not succeeded in defining them sufficiently for a further description. On my first experiment with the first specimen of argon I saw also a fine red ray, analogous to that of hydrogen, but it was not reproduced with the second specimen. The specific rays which I have just mentioned appeared as soon as the violet fluorescence was sufficiently established; they are very beautiful without being displaced by the green or blue fluorescence, but they become invisible when it has disappeared.

I have determined the position of these rays with a single-prism spectroscope, but unfortunately with a feeble dispersion, the experiments made with a spectroscope of

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* The tube then used was the one with which Mr. Crookes's measurements of the argon spectrum were made. It contains absolutely pure atmospheric argon.

great dispersive power having afforded too little light. Under these conditions we view a broad luminous surface, enlightened by a floating fluorescence, where the point of maximum illumination is continually displaced, fatiguing the eye of the observer. The divisions of the scale have been found by means of the two rays of hydrogen C and F, a ray of lithium, the D ray of sodium, and a ray of thallium projected simultaneously with the rays which I am studying.

We obtain thus several points well defined, which enable us to establish by a curve the graduation of the scale and the wave-lengths. Thus, with the aid of M. Mascart, I have determined the following numbers, which must be regarded merely as approximate, the approximation being comprised between 0·005 and 0·003, according to the part of the scale in view.

The yellow ray is very distinctly separated from the ray D, and is nearer to the green region, with an approximate value of 0·579 in place of 0·5896 (D). Still, on operating with an effluve of suitable intensity, this ray is furnished with fine black absorption lines, which indicate the possibility of its resolution.

The green ray is situate near 0·547. It is also furrowed with black lines.

The finest of the violet rays is about 0·438, and the second about 0·436.

None of these rays coincides with that of helium (0·5875), nor exactly with the principal ray of the aurora (0·557), though this last ray seems attributable to fluorescent manifestations analogous or identical, as will be said further.

They correspond, on the contrary, to the brilliant rays of the spectrum of rarefied argon contained in the tube which Prof. Ramsay has sent to the Physical Society of Paris.

The yellow ray may, in fact, be approximated to the number of 0·575, observed by Mr. Crookes, and the ray 0·578 of the aurora.

The green ray corresponds to the number 0·549, or rather to the group of Mr. Crookes, comprised between 0·555 and 0·549. Mr. Crookes's ray, 0·5557, may also be approximated to the principal ray of the aurora.

Lastly, the two violet rays correspond to the numbers 0·433 and 0·430 of Mr. Crookes; they answer also to an important ray of the aurora.

The appearance of these rays of fluorescence, at the atmospheric pressure, would seem to indicate the presence of a hydrocarbon compound of argon of the order of acetylene, or rather of hydrocyanic acid, also in a state of electric dissociation. We further remark their relations, and more generally the resemblance, which the present fluorescence and the rays of argon bear to the fluorescence and the rays of the aurora and of the zodiacal light.—*Comptes Rendus*, cxxx., p. 797.

THE PRODUCTION OF SLATY CLEAVAGE IN AMORPHOUS CELLULOSE.

By CLAYTON BEADLE.

A cellulose coagulum obtained by the spontaneous decomposition of cellulose thiocarbonate when cut in sections by a knife can be readily freed from byproducts by suspending the sections in water. The sheets so obtained consist of 15 per cent of cellulose and 85 per cent of water of hydration. They are of a soft flexible nature, like rubber. We find that the dehydration can be effected by the application of high pressure, and that a compact horny sheet can be obtained by this means containing 10 per cent of atmospheric moisture. The original coagulum is homogeneous, but on the application of pressure, under certain conditions, it is found to exhibit slaty cleavage. On tearing, the edge of the film is found to consist of laminæ of uniform thickness. By varying the mode of applying the pressure and other conditions of treatment, it appears the laminæ may be made to vary in thickness. Sometimes the films are found to consist of two laminæ of equal thickness, and sometimes of a number. Films may be obtained which do not appear to exhibit this property.

It appears that when the material is dehydrated by the application of pressure, that it does not always tend to compact itself with one film, but often into laminæ, and that their thickness varies with the conditions of the pressure, &c.

In order to avoid slaty cleavage in the production of these films, it is necessary to press under conditions that would tend to give rise to laminæ of a thickness greater than that of the ultimate film obtained.

Slaty cleavage may be very much increased by passing the dry thick sheets a large number of times under high pressure between iron rollers.

4, New Court, Lincoln's Inn.

A PREDICTION OF THE DISCOVERY OF ARGON.

By C. J. REED.

The "Remarks on Atomic Weights" of argon and other hypothetical elements, by M. de Boisbaudran, translated from *Comptes Rendus* in the Chemical News, vol. lxxi., p. 116, are very interesting, not only as an evidence of his having predicted the discovery of argon, but also as an illustration of the manner in which different individuals, entirely independent of each other, arrive at the same conclusions.

While M. de Boisbaudran does not publish the reasons for his belief, nor explain the basis of his system, he states that he has found a classification of the elements that enables him to assume the existence of a family of elements, no member of which is hitherto known; that their atomic weights are 20·0945, 36·49±0·08, 84·01±0·02, and 132·71±0·85, assuming O=16. H states further that they should be non-metallic; that the bodies 20·0945 and 36·49 should be relatively abundant in nature, the other two rare.

"The atomicity of the new family should be even, (octo-atomic), but its component elements should be devoid of the faculty of combining with other elements.

"The element 36·40 should be more volatile than sulphur, and the element 20·0946 more volatile than oxygen. Lastly the elements 84·01 and 132·71 should be respectively more volatile than selenium and tellurium."

About ten years ago the writer devised a classification of the elements based solely on the numerical relations between valence and atomic weight.

This classification was described by me in a paper read before the American Association for the Advancement of Science in August, 1885; and in a more complete paper on the "Graphical Representation of the Relation between Valence and Atomic Weight," read before the St. Louis Academy of Science a few weeks later (*Trans. St. Louis Academy of Science*, iv., No. 4).

Plate I. and Figs. 3 and 4 of that paper are reproduced here in fac simile.

In this classification the elements were arranged by locating a point in a plane for each element by rectangular co-ordinates, taking ordinates proportional to the valence, and abscissæ proportional to the atomic weight.

It was found that the loci of two equations, $y=a(x-4)$ and $y=a(x-5)$, pass through or near the points corresponding to more than fifty of the elements whose physical constants are most accurately known; provided the plane is wrapped around a cylinder having its axis parallel with the axis of abscissæ and its radius,—

$$R = \frac{8a}{\pi}.$$

The loci of these equations now become parallel helixes that cut the axis of abscissæ at intervals of sixteen units of atomic weight. The ordinates become arcs of circles formed by planes cutting the cylinder at right-angles to its axis. The axis of abscissæ becomes an element of the surface of the cylinder. The circumference of the cylinder measures eight units of valence. Valence is measured upward from the axis of abscissæ if it is electro-positive, and downwards if it is electro-negative. Elements that exhibit both electro-positive and electro-negative valence (such as chlorine, bromine, iodine, sulphur, selenium, tellurium, nitrogen, phosphorus, carbon, and silicon) show a difference of eight units of valence between the highest electro-positive and the lowest electro-negative values. The locus $y=a(x-4)$ seems to contain mostly artiads, and the locus $y=a(x-5)$

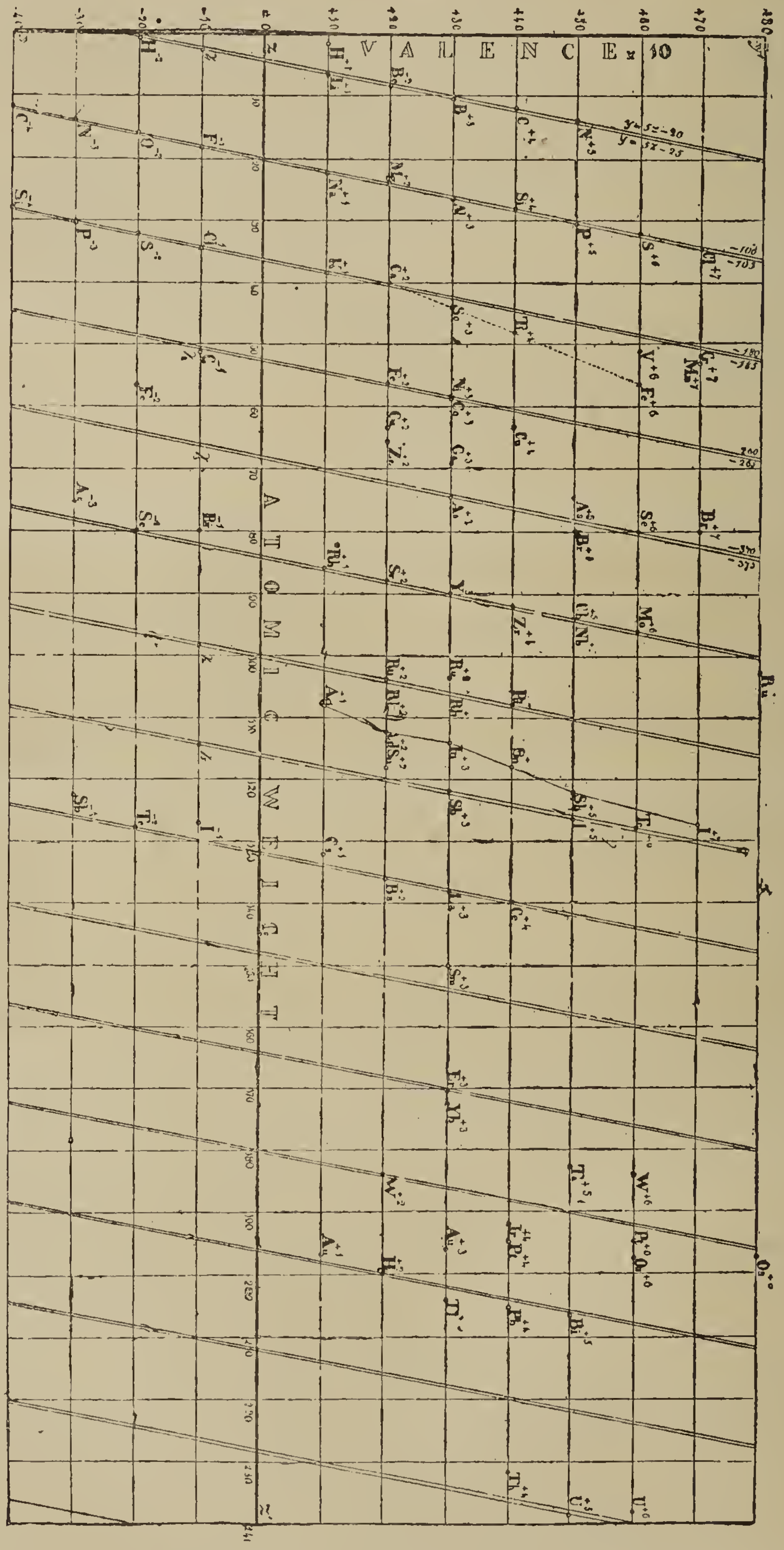

PLATE I. Showing the Relation between Valence and Atomic Weight.

mostly perissads. The complete development of the system would necessitate the existence of four groups or families of artiad elements and four groups of perissads. One of the artiad groups would be a group of undiscovered elements having the following peculiar properties:—

1. The most marked valences of these elements should be either zero or eight; that is, these elements should either combine as octads or else be incapable or nearly incapable of combining with other elements.

2. The total possible number of these elements is fifteen. Their atomic weights are 4, 20, 36, 52, 68, 84, 100, 116, 132, 148, 164, 180, 196, 212, and 228.

3. The only elements of this group that are likely to be found in nature are 4, 20, 36, 84, 132, and 196, possibly 180.

4. The elements of this group should all be highly volatile and probably mon-atomic.

5. Elements 4, 20, and 36 should be comparatively abundant in nature, like most elements of low atomic weight, and they should be non-metallic.

6. Elements 84 and 132 should be comparatively scarce, but not more rare than selenium or tellurium. They should form explosive compounds with oxygen or chlorine.

7. Element 196 should be a metal, heavier and scarcer than gold, and capable of easier reduction to the metallic state; also capable of forming an oxide having the formula RO_4, or alkaline salts having the formula K_2RO_5. The volatile metal osmium agrees very closely with the requirements of this element; while ruthenium may possibly be the element 100.

8. Elements of this group will not combine with one another, and those having low atomic weights will probably not combine with any element, except possibly to form highly explosive compounds with one or two elements. Such compounds could exist only at very low temperatures.

9. Element 20 should bear to element 36 a relation like that of fluorine to chlorine or that of oxygen to sulphur; also 84 should bear to 132 a relation like that of bromine to iodine or that of selenium to tellurium.

The necessity for these elements impressed me very strongly at that time; but I had not the temerity to believe, for the sake of completing my classification, that there could really exist so large a group of elements, all of them entirely unknown, and having such remarkable properties as that of being unable to combine with other elements.

I was content, therefore, to believe this to be a defect in my classification and to merely mark the position of the two most necessary elements on my charts, without indicating that they stood for unknown elements. In Figs. 3 and 4 their positions are indicated at the points marked ±0. The one in Fig. 3, between fluorine and sodium having the atomic weight 20, and the one in Fig. 4 between chlorine and potassium having the atomic weight 36.

I have no desire to claim a post-mortem prediction of argon, but merely to show that I published ten years ago a classification of the elements on which all of M. de Boisbaudran's deductions might have been predicated.

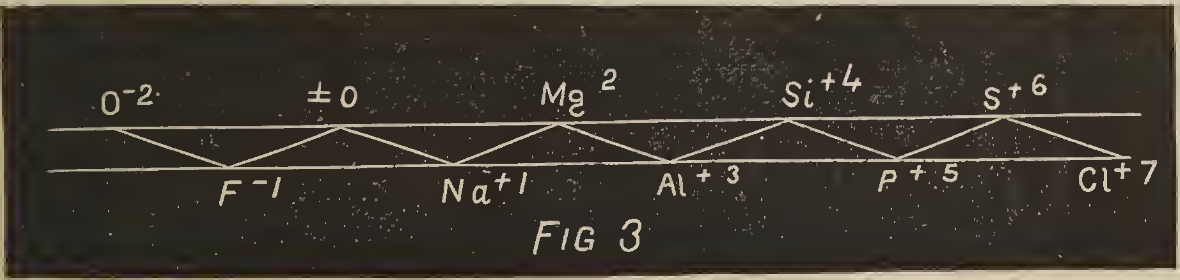

Fig 3

Fig 4

ON THE

ACTION OF ACETIC AND HYDROCHLORIC ACIDS ON SUCROSE.*

By H. A. WEBER and WILLIAM McPHERSON.

While carrying out some experiments with glucose several facts were noticed in reference to the action of acetic and hydrochloric acids on sucrose, which it is interesting to compare with the conclusions reached by Bornträger (*Boh. Zeit. Zucker, Ind.*, 1891, 187; *Bull. Assoc. Chim.*, 1892, 559), Jungfleisch and Grimbert (*Compt. Rend.*, cvii., 390, and cviii., 144), and Ost (*Ber. d. Chem. Ges.*, xxiv.. 1636). Inasmuch as we were working with an entirely different object in view, the conclusions reached were in no way influenced by the conclusions reached by the above writers.

While making an examination of a large number of saccharine products, the writers were led to believe from certain results that complete inversion could be effected by means of acetic acid. This view was contrary to the general opinion of chemists, although as prominent ones as Jungfleisch and Grimbert (*Compt. Rend.*, cvii., 390) claim that acetic acid completely inverts sucrose at 100°, and that it is preferable to other acids, since its presence is without effect upon the levulose of invert sugar. This conclusion was reached from the fact that the specific rotatory power of pure levulose corresponded almost exactly with that of levulose calculated from invert sugar, the inversion being effected by acetic acid. Hydrochloric acid gives a higher invert reading, because, in some way, it acts upon the levulose and increases very perceptibly its specific rotatory power. Exceptions to this view are taken by Maumené (*Journal des Fabricants du Sucre*,—Abstract from March 27th, 1889), who calls attention to the fact that the invert sugar prepared from sucrose by action of acids is not composed of equal parts of levulose

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* *Journal of the American Chemical Society*, vol. xvii., No. 4, April, 1895.

and dextrose. Ost (*Ber. d. Chem. Ges.*, xxiv., 1636) not only denies that acetic acid will produce complete inversion, but also claims that it acts perceptibly upon invert sugar. Ross ("Report of the Association of Official Agricultural Chemists," Bul. 35, Div. of Chem., Dept. Agr., p. 146) states, as the result of a number of experiments, that it was found impossible to secure complete inversion even when 10 per cent glacial acid was used and the flask kept immersed in boiling water for forty-five minutes.

Those who claim that acetic acid does not effect complete inversion base their belief upon the fact that invert sugar, prepared by the action of hydrochloric acid upon sucrose, gives a higher reading than the corresponding solution obtained by the action of acetic acid. It was thought that perhaps acetic acid might form some compound with the constituents of the invert sugar, which might affect the reading of the polariscope. Proceeding upon this assumption, attempts were made to decompose such a compound. In the course of these experiments, which were conducted at great length, certain facts were noted which have been systematised in the following:—

As stated above, Jungfleisch and Grimbert in particular have called attention to the fact that the specific rotatory power of invert sugar, prepared by the action of hydrochloric acid on sucrose, is higher than that of the artificially-made invert sugar. If, however, as Maumené claims, the invert sugar so prepared is not composed of equal parts of dextrose and levulose, then it is possible that the different readings are due to the peculiar compounds formed. In fact one would not expect the readings to be identical under such assumptions.

Accordingly experiments were undertaken to find out, if possible, whether the hydrochloric acid used in inversion affected in any way by its presence the reading of the invert sugar so prepared. Attempts were made in two different directions.

1. Five hundred c.c, of a normal solution of sucrose (polarising at 99·8) was subjected to inversion in 100 c.c. flasks by adding one-tenth the volume of concentrated hydrochloric acid (sp. gr. 1·19) and heating for ten minutes, regulating the heat so that the temperature, 68°, was reached at the end of that time. These solutions were all poured into a large flask and thoroughly mixed, so as to obtain a perfectly uniform solution. Exactly 55 c.c. of this solution were transferred to a 100—110 c.c. flask, the flask filled to the mark with water, the solution thoroughly mixed and polarised. The experiment was repeated with the addition of 5 c.c. of the same acid used in the inversion, previous to filling to the mark with water; again repeated with the addition of 10 c.c., 15 c.c., and 20 c.c., respectively. Since the same solutions, same flasks, and polarising tubes were used, and the temperature of the solutions did not differ more than 0·5°, corrections being introduced for this variation, the chances of error in manipulation were very slight. The following readings, expressed in divisions of cane-sugar scale, were obtained for the various solutions (temperature = 20°):—

Invert sugar (containing 5 c.c. of acid) ..	−33·00
Invert sugar + 5 c.c. additional acid ..	−33·90
Invert sugar + 10 c.c. additional acid ..	−34·65
Invert sugar + 15 c.c. additional acid ..	−35·60
Invert sugar + 20 c.c. additional acid ..	−36·40

The reading is seen to increase with the addition of the acid, thus agreeing with the conclusion of Gubbe (*Ber. d. Chem. Ges.*, xviii., 2207). Moreover, the deviations caused by the addition of the different amounts of acid are fairly constant, varying from 0·75 to 0·95, or an average of 0·85. It was hoped that sufficiently uniform results could be obtained to allow the graphic representation, so that an estimate could be made on the effect of the original 5 c.c. of added acid to bring about inversion. Since, however, the addition of a second, third, fourth, and fifth 5 c.c. of acid each increases the reading of the invert sugar approximately 0·85, then we may conclude, with some probability, that the original 5 c.c. of acid which effected the inversion would increase the reading by that amount.

2. Attempts were also made to solve the problem by neutralising the acid present in the invert solution by the action of sodium carbonate.

Bornträger (*Boh. Zeit. Zucker Ind.*, 1891, 187) has called attention to the fact that the rotatory power of the neutralised solution is higher than that of the corresponding acid solutions. By the addition of sodium carbonate, however, not only is the acid neutralised, but a corresponding amount of sodium chloride is thereby added. Readings were taken first to find out the effect of the addition of the sodium chloride. Then, by comparing this with the variation caused by neutralisation with sodium carbonate, the effect of the acid could be deduced.

Five hundred c.c. of inverted sugar solution were prepared as described above. It was found that 3$\frac{3}{10}$ grms. of pure dry sodium carbonate were necessary to neutralise the acid (5 c.c.) present in 55 c.c. of this solution. The experiments were conducted as in the above: 55 c.c. of the solution were transferred to a (100—110) flask, neutralised with sodium carbonate, the flask filled to the mark, the solution mixed thoroughly and polarised. The duplicates agreed within the limit of error in reading. The average readings on cane-sugar scale were as follows (temperature = 20°):—

	Triplicates.		
	1.	2.	3.
Original solution	−33·1	−33·0	−33·20
Original solution + 3·3 grms. sodium carbonate (neutral) ..	−33·7	−33·7	−33·85
Original solution + 6·6 grms. sodium carbonate	−36·2	−36·0	−36·30

The last reading was taken in order to compare the effects of the addition of sodium carbonate before and after neutralisation. It is thus seen that, while the reading of the normal solution is increased 0·6° by the addition of the necessary amount of carbonate to neutralise the acid, the subsequent addition of a like amount increases the reading 2·5°. Before ascribing this difference in reading to the effect of the acid, it is necessary to find whether or not the sodium chloride, formed by the addition of the sodium carbonate to hydrochloric acid, affected the reading.

Experiments were conducted with the same solution used above: 55 c.c. of the solution were introduced into the 100—110 c.c. flask, and the amount of sodium chloride corresponding to 3$\frac{3}{10}$ grms. of sodium carbonate, or 3·65, added, the flask filled, and the solution polarised as before. The average readings on cane-sugar scale, agreeing within 0·1°, are:—

Original solution	−33·1	−33·15
Original solution + 3·65 grms. sodium chloride	−35·1	−35·10

Since, then, the effect of the sodium chloride was to increase the reading 2°, the acid remaining unneutralised, while the reading was only increased 0·6° by the addition of the same amount of sodium chloride, the acid being neutralised at the same time, the difference 1·4° may presumably be attributed to the action of the acid present.

This result is higher than the one deduced from the direct addition of acid given above, but it is undoubtedly the more correct of the two. It would thus seem that the acid undoubtedly increases the rotatory power, the probable increase of reading being about 1·4° on the direct scale for the normal solution.

Similar experiments were next conducted in order to find out the effect of acetic acid. The strength of the acid used may be inferred from the fact that 5 c.c. of it required for neutralisation 3·05 grms. of dry sodium carbonate. The normal solution of sucrose was heated at 100° with one-tenth volume of this acid for about one hour, experiments showing that continued heating had but little effect upon the reading. By this treatment a reading for the normal solution was obtained on an average of 2° lower than when hydrochloric acid was used as the agent of inversion. The same solution which gave a reading of −33·1° when hydrochloric acid was used gave a reading of −31·1 when treated with acetic acid under the above conditions.

Experiments performed to discover whether the subsequent addition of acetic acid would affect the reading, gave the following results, on cane-sugar scale:—

Original invert solution (temperature 20)	−31·10	−31·0
Original invert solution + 10 c.c. additional acetic acid	−30·85	−30·8

The second reading is the reading obtained from a solution exactly the same as the first 10 c.c. of acetic acid being introduced.

It thus appears that while hydrochloric acid increases the reading by its presence, acetic acid increases it by a small but perceptible amount. This result agrees with Ost, who criticises the statement of Jungfleisch and Grimbert that acetic acid has no effect upon invert sugar. In order to test this further, the acid was neutralised by sodium carbonate and the difference of reading noted. This result, united with the effect due to the introduction of the sodium acetate formed, gave the means of finding the effect of the acid.

The experiments were conducted as in the above, using same solution, same flask, and same polarising tubes. The following are the results obtained, on cane sugar on scale:—

Original solution (temperature 20°) ..	−31·20	−31·1
Original solution + 3·05 grms. sodium carbonate (neutral)	−32·65	−32·6
Original solution + (3·05 × 2) grms. sodium carbonate	−34·80	−34·8

A marked difference is noted here as compared with similar experiments with hydrochloric acid. The neutralisation of the hydrochloric acid increased the reading only 0·6°, while the neutralisation of the acetic acid increased the reading over twice the amount, or 1·5°. The subsequent effects of the sodium carbonate upon the two solutions agree very well, being an increase of 2·5 in the case of hydrochloric acid against an increase of 2·2° in the case of acetic acid. This difference of 0·3° in the reading is accounted for by the fact that 3·3 grms. of sodium carbonate were added in the hydrochloric acid solution, while only 3·05 grms. were added in the acetic acid solution. If correction be made for this difference, the increase in readings differ only by 0·1°.

It was necessary also to find out the effect of the sodium acetate formed by the neutralisation of the acetic acid by sodium carbonate. The readings on the cane-sugar scale were as follows:—

Original solution (temperature 20°) ..	−31·1	−31·1
Original solution + 4·72 grms. sodium acetate	−32·4	−32·4

The sodium acetate used was the pure anhydrous salt.

It is thus seen that while the sodium carbonate increased the reading 1·5°, the introduction into the original solution of the same amount of sodium acetate as was formed increased the reading but 1·3°. The difference of 0·2° must be due to the presence of the acid.

The conclusion that the acetic acid by its presence lowers slightly the reading is confirmed by the fact that by the use of a weaker acid a maximum reading of −31·3° was obtained.

As might be expected, the introduction of hydrochloric acid into a solution inverted by acetic acid increases the reading in a corresponding degree.

It is thus shown that the effect of hydrochloric acid upon a solution of invert sugar is to increase the reading, while acetic acid has an opposite effect. Moreover, the experiments show that the probable increase in reading due to hydrochloric acid under the conditions mentioned is 1·4°, while the probable decrease in reading due to acetic acid is 0·2°. In other words, if these two acids produced the same effects upon being heated with sucrose, there would still be a difference of reading of 1·6° due to the presence of the acid. This agrees fairly well with the actual difference observed.

In the light of these experiments, it may be of interest to notice the question so often discussed, "Does acetic acid effect complete inversion?" If we suppose that no acid effects complete inversion unless it gives a reading such as that obtained by using hydrochloric acid, then most certainly acetic acid does not invert completely. If, on the other hand, we adopt as the reading of the invert solution the reading of the acid solution, corrected for the effect produced by the presence of the acid, then acetic acid gives more nearly the correct invert reading, and it is correct to affirm that acetic acid does invert sucrose completely.

Finally, the above results indicated that when Fehling's solution is used in the place of the polariscope, it would be a matter of indifference whether acetic or hydrochloric acid was used to effect the inversion of the sucrose. Experiments showed this to be true. Two solutions containing the same amount of sucrose were inverted with hydrochloric and acetic acids respectively. After inversion exactly 11·7 c.c. of each solution were required to reduce 10 c.c. of Fehling's solution. Moreover, when Fehling's solution is used for the determination of sucrose in presence of dextrin or commercial glucose, acetic acid is preferable to hydrochloric acid as the agent of inversion, since the process requires no attention, and the error introduced by the hydrolysis of dextrin is less even when the most favourable method of inversion is used, viz., heating for ten minutes, regulating the temperature so as to reach 68° at the expiration of that time.

ARRANGEMENT FOR MEASURING OUT LIQUIDS.

By F. F. SKINNER,
With the Cochrane Chemical Co., Boston, U.S.A.

Whenever it becomes necessary to measure out a given volume of liquid with a pipette, and the same operation is to be repeated a number of times in succession, and the liquid to be measured is volatile and offensive, like gas-liquor, strong ammonia, hydrochloric and nitric acid, &c., more or less of the vapours are thrown into the mouth, causing at least an unpleasant taste, to say nothing about the possibility of getting the liquid itself into the mouth, with consequent risk to comfort and health.

The following arrangement is intended to remedy these objections:—

The pipette is, by means of rubber tubing, connected with a glass Y-tube, one limb of which, A, Fig. 1, is in communication with the filter-pump, or, when this is not convenient, with an aspirator bottle placed on a high shelf near by. Over the other limb, B, of the Y-tube is slipped a short piece of rubber tubing, and, like A, is closed by a glass drop as indicated in Fig. 2. Place the vessel containing the liquid to be measured under the pipette in such a manner that the latter dips under the liquid; now squeeze the glass drop at A, and the liquid will rise in consequence of the suction of the filter pump or aspirator; when it has reached the mark, which is easily done in one operation with a little practice, or is a little above it, the drop is released, and adjustment to the mark is made by cautiously squeezing the drop at B. This done, remove the vessel containing the liquid, and place under the pipette the vessel intended to receive the measured liquid; then squeeze the drop at B until the required amount of liquid has run out. The pipette is easily rinsed out, when necessary, by repeating the operation once or twice before measuring out.

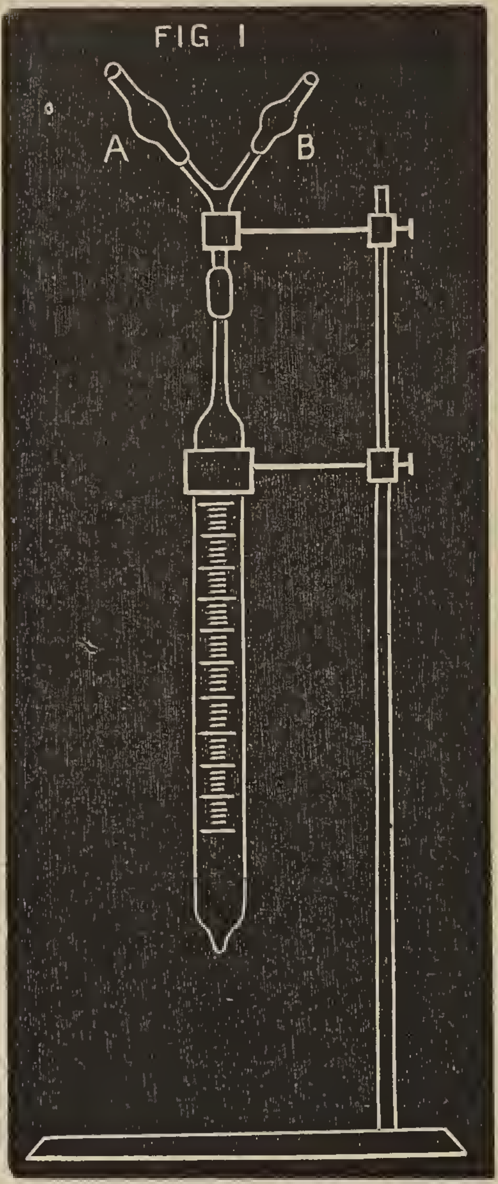
FIG 1


FIG 2

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Anniversary Meeting, March 27th, 1895.

Dr. Armstrong, President, in the Chair.

The President, in opening his Address, referred to the fact that its delivery marked the close of an official connection with the Society maintained during twenty years —a period of great activity in the history of the Society, during which the number of Fellows had increased from 800 to nearly 2000.

The first subject considered was the Faraday lectureship, which he remarked had been described as "an institution that in its most characteristic features is without parallel elsewhere," by Professor Odling, who, moreover, had said, "that having regard to the great name with which it is associated, we cannot doubt that the nomination to this lectureship will ever be held in high esteem." This very fact made the appointment one which occasions great perplexity. Having failed to induce Professor Emil Fischer to deliver the lecture, the Council had been led to fully discuss the matter and to arrive at the conclusion that it would be desirable to break through the practice originally initiated by the Council, and hitherto adhered to, of inviting only foreigners to deliver the lecture. Since this decision was arrived at, circumstances had arisen which had led to an even more novel departure. All were aware that Lord Rayleigh and Professor Ramsay had recently successfully effected the separation of a hitherto unrecognised constituent from the atmosphere, a discovery which was justly regarded as one of the most remarkable ever made in chemistry—but this was no chance discovery. On the contrary, it was the outcome of labours carried out with unwearied perseverance and patience and with consummate skill by Lord Rayleigh during many years past. After tracing the history of the discovery, the President proceeded to say that no chemist could fail to be impressed by Lord Rayleigh's work. Recognising its extreme value, the Council had decided to appoint Lord Rayleigh Faraday lecturer, and to request his acceptance of the medal in recognition of the important service which he had rendered to chemical science by his discovery of argon. They did not ask that he should give a lecture, but made the award of the medal in this special manner in order to mark their sense of the value of his labours, and especially of the example he had set. There was, however, reason to hope that Lord Rayleigh will be prepared to address the Society on the subject of argon.

The President then presented the Faraday Medal to Lord Rayleigh "in recognition of the services he had rendered to chemical science by the discovery of Argon."

Lord Rayleigh said that, in returning his thanks to the Society, he was somewhat embarrassed, because he felt that there ought to be another standing at his side. It was true that his researches, to which the President had referred, upon the densities of gases had rendered it almost certain that a new gas of some sort was concerned, and probable that the new gas was in the atmosphere. But from this point to the isolation and examination of argon was a long step, and the credit for it must be shared equally between Professor Ramsay and himself. In some quarters there had been a tendency to represent that antagonism existed between chemists and physicists in the matter, though such a thought never entered his mind. Professor Ramsay was a chemist by profession, while he himself had dabbled in chemistry from an early age, and had followed its development with a keen interest.

Being called on by the President, Professor Ramsay made a communication of the discovery of helium in clèveite. (See Chemical News, vol. lxxi., p. 151).

Mr. Crookes then gave an account of the spectrum of the gas from clèveite. (See Chemical News, vol. lxxi., p. 151).

Continuing his Address, the President said that the Society had lost an old and faithful servant in the collector, Mr. Hall, who last summer retired on a pension from the Society after being twenty-five years in its employ.

The opportunity had been taken to institute changes in the paid staff of the Society which had long been advocated by the officers but postponed mainly on financial grounds. A collector being no longer necessary, it had been decided to appoint an Assistant-Secretary, who should also act as assistant to the Treasurer and as Librarian. They had been successful in securing the services of Mr. Robert Steele, formerly a science master at the Bedford Modern School.

The fusion of the offices of Assistant-Secretary and of Librarian, effected with the object of securing the constant attendance of the Librarian, had led to the termination of Dr. Thorne's official connection with the Society; on behalf of the Council, he desired to express the warmest thanks to Dr. Thorne for the assistance he had rendered as Librarian since the death of Mr. Watts.

The numerical strength of the Society was as follows* :—

Number of Fellows, March 31, 1894		1962
,, ,, since admitted..		118
		2080
Removed on account of non-payment of four annual subscriptions	24	
Do. three annual subscriptions	33	
Withdrawn	27	
Deaths	17	
		101
Number of Fellows, March 31, 1895		1979
Foreign Members		30

These statistics were by no means satisfactory. Not only was the number admitted smaller than usual, one reason being that 23 who had been elected had failed to satisfy the conditions on which admission into the Society was granted, but an unusually large number had declined to comply with the By-laws and the Treasurer's just demands, and, therefore, were removed from the register. (The names of those who have thus, of their own act, ceased to be Fellows of the Society were then given).

The Society was fortunate in having been deprived of only seventeen of its Fellows by death, viz.:—Ashwell, J. R.; Barratt, Alex.; Beauchamp, Maj.; Board, G.; Carteighe, J.; Dunne, B. L.; Gill, C. H.; *Hughes, F. R.; Johnson, F. R.; Morris, J. E.; Nason, Prof. H. B.; Salet, G.; Twining, A. H.; White, A; Wright, C. A.; Evans, N.; Thornthwaite, W. H.

This list contains the name of one of the original Fellows of the Society, F. R. Hughes, so that now but one remains—Lord Playfair. The decease of Dr. Alder Wright at so early an age was especially to be regretted.

Three foreign members had died during the year—Marignac, v. Helmholtz, and Josiah P. Cooke. Prof. Clève had undertaken to commemorate the work of the first of these, and especially to discuss the present state of our knowledge of the chemistry of the rare earths, a subject to which Marignac devoted particular attention. Prof. Fitzgerald, F.R.S., in like manner had consented to deal with that part of the work of v Helmholtz which was of interest to chemists, viz., electrolysis and the theory of vortex atoms.

Reference was made to a somewhat virulent outbreak of the black-balling mania which affected one of the elections. Having made special enquiries with reference to those who were rejected, he was satisfied, said the President, that they were, in the majority of cases, the victims of unjust prejudice.

The Assistant-Secretary was engaged in verifying the register of Fellows, and, as illustrating the difficulties, it might be mentioned that no fewer than ninety-eight Life Fellows had not responded to the request for their present addresses.

The number of communications made to the Society during the year was 132.

Eighty-three papers were published in the *Transactions* for 1894, occupying 1039 pages; whereas in the preceding year 104 papers were published, occupying 1432 pages.

The Index to the *Transactions*, *Proceedings*, and *Abstracts* occupies 149 pages, and contains upwards of 11,000 entries.

Referring to the labours of the Editors in connection with the *Transactions* and *Abstracts*, the President said that not only the Council but all the Fellows must very fully recognise the great value of the work which is done for the Society by both gentlemen.

Taking into consideration the increase in the size of the *Journal* and its great value, the Council had resolved to increase the sale price to 40 shillings per annum after this year.

Among other topics, reference was made to the issue of abstracts of physical papers by the Physical Society; also to the federation of the various Brewing Institutes, and the issue by them of a Journal, which, besides original matter, was to contain abstracts of papers of special interest to those engaged in the brewing industry.

The technical portion of the address dealing with the ionic dissociation hypothesis and the correlation of structure with function, among other matters, having been taken as read,—

Sir Frederick Abel proposed a vote of thanks to the President, coupled with the request that he allow his Address to be printed. Dr. W. H. Perkin seconded the motion, which was carried by acclamation. The Presieent having thanked the meeting,—

Professor Thorpe, the Treasurer, gave an account of the Balance Sheet, which he laid before the Society, duly audited.

Scrutators were appointed, and a ballot was then taken for the election of officers and Council for the ensuing year; the following were subsequently declared elected:—

President—A. Vernon Harcourt, M.A., LL.D., D.C.L., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, LL.D., Ph.D., F.R.S.; A. Crum Brown, D.Sc., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Lord Playfair, K.C.B., Ph.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents — E. Atkinson, Ph.D.; Horace T. Brown, F.R.S.; F. R. Japp, M.A., Ph.D., LL.D., F.R.S.; Ludwig Mond, F.R.S.; C. O. Sullivan, F.R.S.; W. C. Roberts-Austen, C.B., F.R.S.

Secretaries — J. M. Thomson; W. R. Dunstan, M.A., F.R.S.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—T. E. Thorpe, LL.D., F.R.S.

Other Members of Council—P. P. Bedson, D.Sc.; B. H. Brough; H. B. Dixon, F.R.S.; Bernard Dyer, D.Sc.; R. J. Friswell; O. Hehner; F. S. Kipping, Ph.D., D.Sc.: H. McLeod, F.R.S.; W. A. Shenstone; T. Stevenson, M.D.; W. P. Wynne, D.Sc.; S. Young, D.Sc., F.R.S.

NOTICES OF BOOKS.

The Analysis of Beers, Spirits, and Vinegar. A Guide to Decisions and Opinions on Beers, Spirituous Drinks, Liqueurs, Arrac, Rum, Cognac, and Vinegar. (Die Analyse der Biere, Spirituosen, und des Essigs. Leitfaden zur Beurtheilung und Begutachtung von Bieren, Spirituosen — Brantweinen, Likören, Arrak, Rum, Kognac — und Essig). Compiled by H. A. Blücher, Sworn Chemist and Judicial Expert. With 25 Woodcuts in the Text. Crown 8vo., pp. 291. Kassel: Brunnenmann.

This work is the second volume of a series of analytical pocket-books giving indications for an exhaustive examination or a decision on important products which enter into human diet.

The author, H. A. Blücher, belongs to a class of analysts who have no representatives in Britain, that is the "vereideten chemiker," *i.e.*, scientific chemists sworn to give accurate decisions and reports on any question submitted to them by the Court. They are, we believe, not "called" by either of the litigants, but are rather the scientific assessors of the Bench.

The present volume is a concise but thorough-going manual. The introductory part speaks of the manufac-

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* This statement has been corrected to March 31, 1895.

ture of beer, its defects and diseases, and its preservation. The analytical part deals, firstly, with the raw materials, water, barley, malt, hops, wort, and yeast.

The author, like German authorities in general, considers soft waters, free from organic matter, preferable for brewing purposes, though he admits that gypsiferous waters may expedite the clearing of worts.

Next follow general and special methods for the analysis of beer. The author then shows the general principles to be kept in view in official reports on malt-liquors, with especial reference to substances which may be possibly present, but which are to be at once condemned. Such are boric and salicylic acids. It is curiously remarked that though salycilic acid must be objected to in beers for German consumption, it is admissible in such as are destined for exportation. The maximum limit for glycerin in beer is stated as 0·25 grm. in 100 grms.

Spirituous liquors are classified as spirits for ordinary consumption, such as grain- and potato-whiskey, gin, and inferior brandy. A higher grade includes arrack, rum, and cognac. The first-mentioned of these spirituous liquors contains 48 to 54 per cent by weight of alcohol; in rum the proportion reaches 65 to 73; and in cognac 40 to upwards of 60.

Among the substances which justify a condemnatory decision, aloes and gamboge find a deserved place.

The composition of absinthe is given, but there is not a word of condemnation or of caution concerning this most objectionable of all alcoholic liquors. It is remarkable that the "Temperance" party in Britain, active and watchful as they are, have never made any protest against its importation or sale in these realms.

It is stated, doubtfully, that methylic alcohol may be found in arrack and rum. Formic acid is also a questionable ingredient.

Grain- and potato-spirits are to be distinguished by their odour; 20 c.c. of the sample are mixed with 0·2 potassium hydrate, dissolved in a drop, well shaken up, and slowly evaporated to 6 grms. This residue is then shaken up in a closed test-tube, with an equal volume of dilute sulphuric acid. On opening the tube the characteristic fusel smell of grain-spirit, or the disgusting odour of potato-spirit, may be plainly recognised and distinguished.

This work will prove very useful to manufacturers of and dealers in alcoholic liquors, and still more to public analysts.

A Primer of Evolution. By Edward Clodd, President of the Folk Lore Society. With Illustrations. 12mo., pp. 186. London and New York: Longmans, Green, and Co. 1895.

This is a popular exposition of the process commonly known as evolution, but named by the French, less elegantly though perhaps more correctly, "transformism."

This transformation is traced out in the phenomena of astronomy, of geology, and of biology, vegetable and animal. The great question of chemical evolution, of the formation of our present elements from some possibly antecedent state or states, is not distinctly touched. This deficiency deprives the work, for us, of its main value. We should have been happy to see the author's views on this capital phase of the question. Perhaps Mr. Clodd might have met with some decisive evidence for or against chemical evolution.

The author seems to accept the Darwin-Wallace hypothesis of Natural Selection as the main, if not the sole, agency which has been brought to bear. He seems to disregard the fact that this hypothesis is certainly not gaining ground in the opinion of the scientific world. Nor does he, as far as we can perceive, remind his readers that change is not the universal law of the universe, and that where traced it may be, and often is, in the direction of degradation. This truth might, we submit, have been enforced with the more advantage as the author includes human society in the circle of his speculations, where transformation assumes a phase not of differentiation, but of a movement in the opposite direction.

Agricultural Journal. Published by the Department of Agriculture of the Cape Colony. Vol. viii., No. 5.

This issue contains not a few interesting facts and suggestions.

There prevails in Namaqualand the disgraceful superstition that it is sacrilegious to kill locusts, since they are sacred insects! We doubt if any native race in India could surpass this folly.

Canary seed (*Phalaris canariensis*) is recommended as a useful crop for cottagers; it is well suited to the climates of Africa and Australia.

The preservation of potatoes is found practicable by the Schribau process. The tubers are immersed for twelve hours in a 2 per cent solution of sulphuric acid, and then dried.

The world's stock of sheep is given as 583,030,200 head. Of these, there are in the United Kingdom, 33,642,000; Australia, 124 845,600; South Africa, 35,759,935; and Asia (chiefly India), 53,401,579. In the La Plata countries there are more than 135,000,000.

The contagious American peach-disease, the yellows, does not exist in Africa. Irrigation should never be applied by means of water left round the stem of the tree.

A process has been discovered by means of which the fruit of the loquat may be rendered seedless. It is suggested that the peach, nectarine, and apricot might be improved in a similar manner.

Bee-owners in various parts of the colony are greatly exercised by the ravages of the "bee-pirate,"—a *Philanthus* near of kin to the *Philanthus apivorus* of Europe. Here is scope for inventors!

The Most-frequently Used Apparatus and Utensils for Chemical Laboratories. Drs. Peters and Rost, Manufacturers of Chemical Apparatus and Utensils, No. 27, Sophie Charlotten Strasse, Charlottenburg, near Berlin. London Agency: Imperial Wharf, 46, Bankside, S.E.

Among the novel specialities here mentioned and figured is a shaking arrangement which has not only a lateral but a rotatory movement, and requires but little power; a diazotising funnel; a dyeing apparatus and a yarn-dyeing appliance, both for testing purposes. There is also a patent cork-squeezer for laboratory purposes, which presses and rolls the cork at the same time.

The firm also offer for sale collections of fluorescent solutions, of micro-chemical reagents, preparations for microscopic study of alkaloids, of coal-tar dye-wares, physiological chemicals, vegetable drugs, &c., for biological and chemical demonstrations.

CORRESPONDENCE.

ON THE
DIMINISHING OF PIPING IN CRUCIBLE-STEEL INGOTS CAST FOR TOOL MANUFACTURE.

To the Editor of the Chemical News.

Sir,—I thank you very much for inserting the note on my system of casting and forging ingots, which seems to me by experiment to be simple and effective. My system, in fact, turns the ingot from an upright position, as now made, to a horizontal position; and, besides, the section of the ingot, 9 in. × 9 in. is much bigger than are the ingots ordinarily, 4 in. × 4 in., the height of the ingots being respectively—H, 3½ in. in my system; H, 16 in. in high ingots. The weight of the metal in both cases is about ⅔ cwt. (the charge of my crucible). In the ordinary way we obtain a funnel with a long tube (the pipe), whereas in my system the pipe is cup-formed.

There is a mistake in the dimensions of the mould as given; instead of 6 in. × 6 in. (the dimension given in the design with the walls of the mould), it must be 9 in. × 9 in. (the dimension of the mould inside), and instead 9 in. the height 6 in., counting the place for the lid (2 in. thick). The resulting ingot, roughly speaking, is 9 in. × 9 in.; height $3\frac{1}{2}$ in.; = $\frac{2}{3}$ cwt. of steel.

In a hurry one is liable to make mistakes, and I feel that I am to blame for this. Will you kindly publish this letter as a correction.—I am, &c.,

SERGIUS KERN.

House 2, Lodge 36.
Leshtoukoff Pereoulok,
St. Petersburg, April 11, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 15, April 16, 1895.

Observations on Argon: Fluorescence Spectrum.—M. Berthelot.—(See p. 212).

Minimum Temperature Registered this Winter at the Summit of Mont Blanc.—J. Janssen.—The minimum temperature observed has been −43°.

Researches on Assimilable Nitrogen and on its Transformations in Arable Soil.—M. Pagnoul.—The experiments of last year lead to the following conclusions:—1. The rains, if abundant, may cause, on rich soils, a considerable loss of nitric nitrogen. 2. Vegetation covering the soil may hinder this loss, as has been already established by M. Dehérain. 3. Carbon disulphide, without killing the nitric ferment, arrests its action for the moment. 4. The ammoniacal forms seem to be a transitory state which organic nitrogen assumes when passing to the nitric state, and the carbon disulphide merely arrests it momentarily in this stage of its transformation. 5. The nitrous form may also be a transitory unstable state of the nitrogen passing from the organic to the nitric stage.

Presence of Helium in Clèveite.—P. T. Clève.—(See p. 212).

Definite Combinations of Metallic Alloys.—H. Le Chatelier.—The author has obtained and examined the tin-copper alloy, $SnCu_3$; the zinc-copper alloy, Zn_2Cu; the aluminium-copper, AlCu; and the chrome-zinc.

Aliphatic Aldehyds.—Louis Henry.—The intensity of the aldehydic character in the series examined by the author increases with the rise of the molecular weight.

Action of the Halogens upon Pyrocatechine.—H. Cousin.—The author has prepared and examined a trichlorocatechine, $C_6H_3Cl_3O_2$, and a bibromocatechine, $C_6H_4Br_2O_2$.

Siccative Properties of Fatty Matters in General, and their Transformation into Elastic Products Analogous to Lincxine.—If the distinction of the vegetable oils into driers and non-driers is exact, it is with the reservation that the oxidation of these oils is effected only at the ordinary temperature. The transformation into an elastic product analogous to that afforded by the drying oils can be effected in a general manner for all oils, vegetable or animal, if they are submitted to a suitable temperature.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 2, 1895.

Safety Valve for a Water Air-pump.—M. Berlemont.—This paper requires the accompanying figure.

Determination of the Molecular Weights of Liquids: Application to the Carbides.—Ph. A. Guye.—The author seeks to demonstrate that the determination of the molecular weight of a liquid may be referred to the knowledge of four constants, *i.e.*, the critical temperature, the critical pressure, and the temperature of ebullition at any given pressure. If this last temperature is referred to the atmospheric pressure, we have only to determine three constants. In certain cases it may be advantageous to determine also the molecular refraction. The author's results are given in the form of three tables.

Researches on the Dissociation of Mercuric Sulphate and Nitrate by Water.—Raoul Varet.—In the action of water upon mercuric sulphate, the reaction produced is that which evolves the greatest quantity of heat. This explains why this salt is decomposed by water into free acid and a basic salt, exothermic reactions; whilst it would be endothermic with alkaline or metallic salts which water does not decompose. In the dissociation of neutral mercuric nitrate by water the reaction ensues which is the least endothermic.

Certain Aluminium Compounds.—E. Schlumberger.—In this lengthy memoir we can merely notice the reactions with textiles and colouring matters. The various colloidal hydrates obtained do not seem able to play the part of mordants. A swatch of calico saturated with aluminium triacetate, and afterwards treated according to the methods used for fixing mordants of alumina, appears to fix the alumina only in a very imperfect manner. If dyed up in alizarin it takes a pale dull rose, not at all like a logwood red. If dyed in logwood it takes merely a dirty violet-grey. If we wish to obtain the reactions of the aluminous solutions with decoction of logwood, care must be taken to compare solutions which do not contain an excess of acid. We then have the following reactions:—*Normal aluminium acetate*, a red violet colour, warm and bright, the liquid remaining clear. *Trialuminium acetate*, dirty reddish grey colour; liquid turbid. Acetate obtained by heating the normal acetate to 150°, freed from excess of acetic acid by prolonged ebullition, remained coloured like onion skin. It has long been known what a pernicious action is exerted upon aluminous mordants, fixed but not yet dyed, by alkaline baths, even if incapable of dissolving alumina, such, *e.g.*, as milk of lime, and the equally degrading action of steam at 100° if prolonged. On reference to the foregoing, we shall find that the conditions destructive to the aluminous mordants are precisely those which favour the formation of trialuminium hydrate and of the more condensed hydrates. It appears, hence, probable that the degradation of the mordant observed in the cases mentioned is due to the formation of hydrates which are incapable of acting as mordants.

Researches on Mercury Nitrates.—Raoul Varet.—Nitric acid, like the sulphuric, picric, acetic, and oxalic acids, but unlike the hydrochloric and hydrocyanic acids, along with mercury oxide is displaced by the latter acids completely or appreciably.

Ethyle 3-Aminoanticrotonate and its Homologues.—R. Thomas-Mamert.—The author expounds the formation of the aminic derivative of acetylacetic ether. He shows that the stereoisomerism of the crotonic and isocrotonic acids must be necessarily and definitely admitted.

Combination of Hexamethyleneamine with Silver Nitrate, Chloride, and Carbonate.—M. Delepine.—It is remarkable to observe the combinations of a base with silver chloride and carbonate.

Researches on Pectase and Pectic Fermentation.—G. Bertrand and A. Mallèvre.—The ferment does not alone coagulate pectine. It effects this transformation only in presence of a soluble salt of calcium, barium, or strontium. The coagulum formed is not, as formerly supposed, pectic acid, but an alkaline-earthy pectate.

Volumetric Determination of the Mineral Salts of Zinc.—L. Barthe.—This paper will be inserted at some length.

MISCELLANEOUS.

Common Salt as a Fungicide. — According to the *Cape Agricultural Journal*, crops of wheat grown on soils containing 700 lbs. of chlorine in the soil, down to the depth of 6 inches, have been found free from rust.

The Cremometer. — MM. P. Cazeneuve and E. Haddon find, from a series of careful experiments, that the indications of the cremometer are not trustworthy for samples of milk which have been Pasteurised at 98° to 100°, with exclusion of air.—*Journal de Pharmacie et de Chimie.*

Royal Institution. — The Annual Meeting of the Members of the Royal Institution of Great Britain was held on May 1st, at the house of the Institution in Albemarle Street, Sir James Crichton-Browne presiding. The Annual Report of the Committee of Visitors for the year 1894, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Real and Funded Property now amounts to above £102,000, entirely derived from the Contributions and Donations of the Members, and of others appreciating the value of the work of the Institution. 62 new Members were elected in 1894, and 63 Lectures and 19 Evening Discourses were delivered in 1894. The Books and Pamphlets presented in 1894 amounted to about 242 volumes, making, with 578 volumes purchased by the Managers, a total of 820 volumes added to the Library during the year. Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors for their valuable services to the Institution during the past year. The following gentlemen were unanimously elected as Officers for the ensuing year:—President—The Duke of Northumberland, K.G. Treasurer—Sir James Crichton-Browne. Secretary—Sir Frederick Bramwell, Bart. Managers—Sir Frederick Abel, Bart., K.C.B.; Captain W. de W. Abney, C.B.; the Right Hon. Lord Amherst; Mr. William Anderson; Sir Benjamin Baker, K.C.M.G.; Messrs. John Birkett, William Crookes, Edward Frankland, Charles Hawksley, John Hopkinson, Alfred Bray Kempe, George Matthey; the Right Hon. the Marquis of Salisbury, K.G.; Messrs. Joseph William Swan, Basil Woodd Smith. Visitors — Messrs. John Wolfe Barry, C.B., Charles Edward Beevor, M.D., Arthur Carpmael, Carl Haag, Victor Horsley, Hugh Leonard; Sir Joseph Lister, Bart., M.D.; Messrs. Lachlan Mackintosh Rate, Alfred Gordon Salamon, Felix Semon, M.D., Henry Virtue Tebbs, Silvanus P. Thompson, John Westlake, Q.C.; His Honour Judge Frederick Meadows White, Q.C.; and Sir William H. White, K.C.B.

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Action of Hydrogen Peroxide on Ammonium Sulphide.—On the 23rd of February last, while removing the contents of his laboratory in Massachusetts, U.S., prior to returning to England, the writer noted two solutions oddly mixed in with apparatus and reagents. They were ammonium sulphide and hydrogen peroxide, the latter being a sample from the Oakland Chemical Co., of New York City. Hence it occurred to him to note their effect, if any, when brought together. The sulphide almost at once turned to an opaque yellow, due possibly to liberated sulphur. There was also a sensible rise of temperature, but the amount was not taken. In about 10 or 15 mins. the liquid got clear again and looked very like unaltered NH_4HS. Probably varying amounts of H_2O_2 would lead to varying results. As the writer has not, at present, the means of continuing his inquiries practically, he would be glad to receive information as to the nature of these changes, if they have already been investigated.—E. Rattenbury Hodges, Upper Holloway, N., April 24, 1895.

MEETINGS FOR THE WEEK.

Monday, 6th.—Society of Arts, 8. (Cantor Lectures). "Recent American Methods and Appliances employed in the Metallurgy of Copper, Lead, Gold, and Silver," by James Douglas.
— Society of Chemical Industry, 8. "The Use of Hot Air in Drying," by C. C. Hutchinson. "The Estimation of Alkaline Salts in Fire Clays, Manures, &c.," by A. Cameron.
Tuesday, 7th.—Royal Institution, 3. "Alternating and Interrupted Electric Currents," by Professor George Forbes, F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30.
— Society of Arts, 4. "Recent Improvements in Designing, Colouring, and the Manufacture of British Silks," by Thomas Wardle.
Wednesday, 8th.—Society of Arts, 8. "The Extraction of the Rarer Metals from their Oxides," by Prof. W. C. Roberts-Austen, F.R.S.
— Geological, 8.
Thursday, 9th.—Royal, 4 30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Liquefaction of Gases," by Prof. Dewar, F.R.S.
— Institute of Electrical Engineers, 8.
Friday, 10th.—Royal Institution, 9. "A Recent Journey in Afghanistan," by the Hon. G. N. Curzon, M.P.
— Physical, 5. "On the Iodine Voltameter," by E. F. Herroun. "A New Method in Harmonic Analysis," by A. Sharp.
— Astronomical, 8.
Saturday, 11th.—Royal Institution, 3. "Music and Musical Instruments of the 16th, 17th, and 18th Centuries," by Arnold Dolmetsch.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1850.

IMMUNITY OF SOME LOW FORMS OF LIFE FROM LEAD POISONING.[*]

By T. W. HOGG.

The earthworms which form the subject of this paper were obtained from the waste bark heap of the Elswick Lead Works. This heap consists principally of the old bark taken from the white-lead stacks, with a small proportion of sweepings from the yards; it now amounts to over 20,000 tons, and is the accumulation of over fifty years.

From the nature of the origin of this heap it is evident that, owing to the continual breaking off of small particles and powder from the brittle corroded sheets the bark will at length become impregnated with a considerable quantity of white-lead; this quantity varies to a small extent in different parts of the heap, but, generally speaking, the bark dried at 100° C. contains from 1·5 to 2·5 per cent of lead calculated as protoxide. Occasionally, however, somewhat larger proportions are met with, owing most likely to the fact that parts of the heap have been burnt, and the loss of the organic constituents of the bark sensibly increases the proportion of lead at those parts.

Away from the surface the bark is in a damp pulpy condition, and has to a great extent been converted into a kind of vegetable mould.

The composition of a good average sample is:—In original state, water = 50·20 per cent; dried at 100° C.:—

Carbon	45·60
Hydrogen	4·40
Oxygen with a small proportion of nitrogen, by diff.	29·50
Mineral matters other than lead ..	18·02
Protoxide of lead	2·48
	100·00

Notwithstanding that this partially decomposed bark heap would seem to offer an abundance of food for many organisms, the presence of so much lead would certainly lead one to suspect that it would not be a desirable residence for any of them.

It has therefore often been a matter of surprise to me to find that, especially in the summer time, this bark heap is a perfect hot-bed of life; it contains quite a considerable variety of organisms, the largest of which is the common earthworm.

I have examined these worms at different times, and have always found large quantities of lead in them. This would naturally follow from the fact that, although they will eat almost anything, even their own kind, they prefer food of a purely vegetable nature; this bark, therefore, undoubtedly supplies them with nutrition, and has, in consequence, ultimately been converted into its present disintegrated condition.

The intestines of the worms are always filled with finely-divided bark, and, if the whole organism is desiccated and dried at 100° C., the quantity of lead found corresponds very closely with that present in the bark itself.

The following are some of the determinations I have made in this way, the lead being stated as protoxide:—

A (1884)	1·85 per cent PbO.
B ,, ...	1·75 ,,
C ,, ...	2·20 ,,
D (1891)	2·45 ,,
E ,, ...	2·48 ,,
F (1895)	2·60 ,,

The earthworms themselves consist of approximately 80 per cent of water and 20 per cent of organic and mineral constituents. From these figures the percentage of lead in the living organism may be obtained as follows:—

A	0·37 per cent PbO.
B	0·35 ,,
C	0·44 ,,
D	0·49 ,,
E	0·496 ,,
F	0·52 ,,

Although this relatively large proportion of lead is present in each worm, the following experiments show that very little of it is retained or absorbed in its organs. Upon three separate occasions several worms had their intestines opened and thoroughly washed out; the quantity of lead was then ascertained in the worm freed from its intestinal matter, each determination being made upon 8 to 10 grms. The results now obtained were 0·009 per cent, 0·018 per cent, and 0·015 per cent respectively. Although this proportion does not appear to be very large, it is enormously greater than that found in any of the organs of the human adult who has died of lead poisoning. It is known that lead is chiefly absorbed by certain muscles and nerves, but for what reason no one has yet determined (Percy, "Met. Lead," p. 526). The most thorough investigation as to the quantity of lead present in the different organs has been conducted by Prof. Bedson ("Thorpe's Dictionary of Applied Chemistry," vol. ii., p. 445). Seventeen different organs were examined, and, although the largest quantity of lead was found in the liver, the largest proportion was present in the grey matter of the basal ganglion, this proportion being only 0·00053 per cent, and only about 1-25th of this proportion was found in the heart.

On account of the small weight of the organs of the earthworm, it would require an enormous number to be dissected in order to determine the relative proportion of lead absorbed by them. I have not made any attempt to do this. I have, however, dissected several, and treated them with a solution of ammonium sulphide to find if any part was specially darkened, and only in the case of the intestinal walls does this appear to take place.

Particular interest is attached to the calciferous glands. Darwin considers that the special function of these glands is to excrete lime. It occurred to me, therefore, to closely examine them, as they might also have something to do with enabling the worm to get rid of the large quantity of lead continually passing through it. Of course the glands are so minute that it would be impossible to determine the lead, if any, in them. On squeezing out the white pulpy matter upon a glass slide, and examining it under the microscope, treatment with ammonium sulphide failed to reveal the slightest evidence of their containing lead in any form. It is evident, therefore, that these worms are able to allow large quantities of lead to be continually passing through them. But it is not impossible that, during the somewhat long period the heap has been in existence, the worms have by successive generations evolved a special type, capable of withstanding the noxious effects of the lead. I should perhaps mention here that large worms are not often met with; they are generally of a very small kind (probably *Lumbricus minor*).

I have tried one preliminary experiment to ascertain the effect of white-lead upon fresh healthy earthworms, and placed several of them in large trays with good soil mixed with 1, 3, 4, and 5 per cent of white-lead; the soil was kept damp by daily adding a little water. These worms all lived for about two months; near the end of

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[*] A Paper read before the Society of Chemical Industry, Newcastle Section, February 28th, 1895.

this time several of them disappeared and the remainder became very inactive, but I think they lost their vigour more through want of food than through any deleterious effect the white-lead had upon then.

We have no means of judging how large a quantity of earth a single worm ejects during the year. Darwin roughly estimates this at 20 ozs. Taking this figure and the ordinary weight of a worm to be about $1\frac{1}{2}$ grms., without any attempt at great accuracy, if a man possessed similar freedom from the noxious effects of white-lead, he would be able to swallow annually ten times his own weight of white-lead, and also to retain continually one pound of it.

In concluding this short paper, I have only intended to bring this subject forward in its present form as an additional instance of the immunity of certain organisms from the action of substances intensely poisonous to others. In connection with this highly interesting subject of immunity, perhaps it may not be out of place to briefly mention that we are now acquainted with organisms that continue to live in that most powerful destroyer of dead organic matter, potassium permanganate; with Algæ that live and are reproduced in arsenical solutions, and also assimilate arsenic from its solutions. There is a bird (*Buceros Rhinoceros*) that is reputed to eat nux vomica with impunity. Certain organisms are not affected much, if at all, by dilute solutions of mercuric chloride; and other more familiar instances will no doubt occur to those interested in such matters.

In connection with this subject I may mention that, some time ago, whilst experimenting with Carey Lea's silver solutions, I observed that moulds and bacteria grow and are reproduced in them after the introduction of a suitable food, and in the presence of so much silver that were it combined to form a soluble salt such as the nitrate, it would be quite impossible for anything to live in it. This latter subject seems to give promise of interesting results, and I may bring it before the Society upon some future occasion.

A CHEAP FORM OF SELF-REGULATING GAS GENERATOR.[*]

By W. W. ANDREWS.

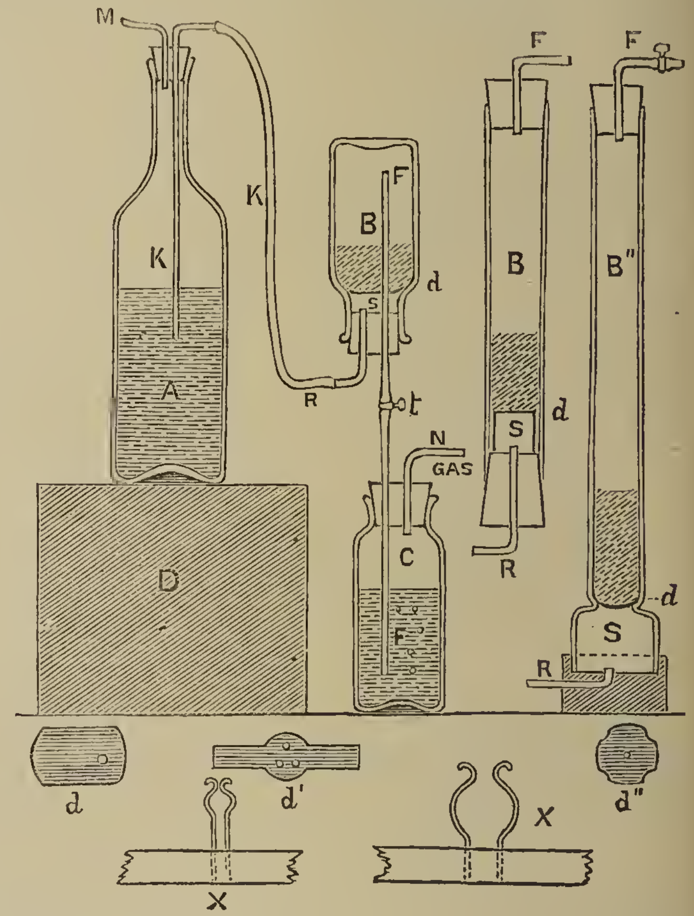
This form of generator is so cheap and easily set up that it makes it possible for every teacher and experimenter in chemistry to have, at practically no expense, a set of generators capable of yielding, whenever called upon, a supply of hydrogen, hydrogen sulphide, chlorine, carbon dioxide, sulphur dioxide, &c. It consists of an ordinary bottle, A, to serve as reservoir for the acid; a smaller bottle, B, which is the generator proper; and C, the familiar wash-bottle. A is closed by a cork holding two pieces of glass tubing; the one, M, just pierces the cork, and the other, K, reaches down a short distance below the surface of the acid and is connected by means of a rubber tube with R, thus forming a syphon leading from A to B, as shown in cut. The tube M is used to start the syphon K R by blowing into A while the stopcock, *t*, is open. F is the exit tube for the gas. The charge of solid in B rests on a shelf of sheet lead, *d*, the width of which equals the diameter of the neck of the bottle, and its length the internal diameter of the bottle. It serves the purpose of securing a space, S, which prevents the extra gas generated, when *t* is closed, from pressing the acid out of the syphon. Instead of a bottle for holding the charge a calcium chloride tube, or an Argand lamp chimney, with its larger end closed with a cork or sunk into a wooden block and cemented with paraffin wax, or even a piece of large-sized tubing may be used. If the last be used the space S is secured by cutting the lead in the shape *d'* and bending it to form a bench to support the solid charge, as shown. *d''* is the shape of the lead support to be used in the calcium chloride tube or Argand chimney. X and X' are the wire springs for holding B to its support, from which it may be lifted or replaced instantly. One is to enclasp the body, and the other the neck of the bottle or one of the glass tubes below the cork.

The advantages of this form of generator are:—

1. Its cheapness. An ordinary fruit-juice bottle and two wide-mouthed eight-ounce bottles will, with the necessary tubing, make one of good capacity.

2. Its convenience and safety. It is strictly self-regulating. If a rubber tube fitted with a glass plug $\frac{1}{2}$ inch long, instead of a stopcock, be used, the gas flows only when the fingers pinch up the rubber along one side of the plug and ceases the moment they are lifted. The apparatus, therefore, is self-closing. It is very easy to re charge either with acid or solid.

3. It ensures a more even quality of gas than the well-known Kipp, and as complete utilisation of the acid as the Koninck generator. When the gas presses the acid back from B, it enters A laden with dissolved solid, and, on account of its greater specific gravity, it falls in a straight line to the bottom, where it spreads out in a dense layer. When the apparatus is again set working the purest acid is drawn from the upper layers. There is, consequently, some advantage in using a tall bottle for A.



4. It may be put together in a form which has all the advantages possessed by the Schanche generator (see *Journ. Amer. Chem. Soc.*, Dec., 1894), making the glass tube R long enough to reach to the top of B, and to curve a little downward, so that the acid may drop on the top of the solid charge and trickle through it. A drainage-tube with stopcock must be inserted into the cork to carry off the used-up acid from the space S. The inverted bottle for B possesses this advantage over the calcium chloride tube or chimney, viz., that owing to the position of the mouth of the gas exit tube, F, solid particles are not so likely to be shot into it when the acid is vigorously attacking the solid charge.

5. The pressure can be regulated at will by placing A at different heights, and this pressure may, at any moment, be reinforced by blowing into A, and the reinforcement held by closing M by means of a rubber tube and pinchcock.

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[*] *Journal of the American Chemical Society*, vol. xvii., No. 4, April, 1895.

VARIATION IN THE AMOUNT OF FREE AND ALBUMENOID AMMONIA IN WATERS, ON KEEPING.

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

In the course of an investigation into the quality of the Sydney Water Supply, 1875, I had noticed variations in the amounts of ammonia after keeping, and in order to obtain satisfactory and trustworthy data with respect to such changes, *i. e.*, as far as they were determinable by Mr. Wanklyn's process, samples of water were put up with the utmost care, and the amount of ammonia determined from time to time, a separate bottle being opened for each determination.

When waters were artificially made impure, the admixture was effected in a large glass pan, well stirred and otherwise mixed, and then transferred to clean clear quart bottles which were filled to the top and the excess squeezed out by the stopper.

The results, in the following Tables, show very clearly that, in some cases, the amounts of free and albumenoid ammonia increase and then decrease, and occasionally increase again; these changes are much more strikingly shown in the curves than in the tables; until decomposition and other natural changes have taken place, the potassium permanganate process fails to set free a large proportion of the albumenoid ammonia from the organic matter, so that a water might wrongly be declared pure if examined when freshly collected, or after lengthened keeping.

These following series of experiments were carried out as far back as 1876 with the aid of my then assistant, Mr. J. M. Muir, afterwards University Demonstrator.

I have hitherto refrained from publishing this investigation as I had hoped to extend the results in other directions, but as it may be some time before additional experiments can be undertaken, I present those already obtained. These, however, as far as they go, show how very important it is that the reports on the analysis of water should state how many days, weeks, or months have elapsed since the samples were collected.

The temperatures given in the table were taken at 9 to

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* Read before the Australasian Association for the Advancement of Science, Brisbane, January, 1895.

Table I.

Nine Bottles each of Garden Tank, Laboratory Tank, and Distilled Water.

(Put up on October 9th, 1876).

Temperature F.				Garden Tank.		Laboratory Tank.		Ordinary Distilled Water.	
				Parts per 1,000,000		Parts per 1,000,000		Parts per 1,000,000	
Morning. °	Evening. °	Nos.	Date. Oct.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.
68	70	1	11	0·01	0·09	0·35	0·184	0·07	0·04
68	70	2	12	0·005	0·042	0·25	0·08	0·09	0·036
68	69	3	13	0·01	0·04	0·24	0·094	0·05	0·03
65	66	4	14	0·01	0·04	0·22	0·11	0·07	0·03
67	67	5	16	0·01	0·054	0·23	0·096	0·04	0·01
71	71	6	17	0·01	0·04	0·23	0·08	0·04	0·005
70	68	7	19	0·005	0·03	0·22	0·06	0·04	0·005
70	70	8	20	0·005	0·02	0·22	0·084	0·03	0·005
71	70	9	21	0·005	0·02	0·21	0·07	0·005 (Nov. 1).	0·005 (Nov. 1).

In all of these, with slight variations, there was a gradual improvement on keeping. The Laboratory tank at the time of these experiments was supplied with rain-water from the slate roof of the main building. The garden tank (underground) was also supplied from the same source. It is noticeable that there are considerable differences between the Laboratory tank and the underground garden tank waters although from the same roof.

Table II.

Five Bottles each of Garden Tank, Laboratory Tank, and Distilled Water.

(Put up on October 18th, 1876).

Temperature °F.				Garden Tank.		Laboratory Tank.		Ordinary Distilled Water.	
Morning.	Evening.	Nos.	Date.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.
67	65	1	Oct. 18	0·005	0·04	0·018	0·07	0·036	0·002
70	68	2	,, 19	0·005	0·03	0·13	0·06	0·03	0·005
72	70	3	Nov. 1	0·005	0·01	0·15	0·06	0·005	0·005
76	78	4	,, 16	0·005	0·01	0·15	0·06	0·005	0·005
71	73	5	,, 20	0·005	0·005	0·14	0·06	0·000	0·005

Note.—Heavy rain fell for about two hours on the morning of the 18th, just before collecting these samples.

Table III.

Seven Botttles each, Garden Tank, Laboratory Tank, and Distilled Water.

(Put up on October 23rd, 1876).

Temperature °F.				Garden Tank.		Laboratory Tank.		Ordinary Distilled Water.	
Morning.	Evening.	Nos.	Date.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.	Free NH_3.	Alb. NH_3.
72	70	1	Nov. 1	0·005	0·01	0·06	0·04	0·005	0·005
72	75	2	,, 21	0·005	0·005	0·04	0·05	0·005	0·005
74	76	3	,, 22	0·005	0·005	0·04	0·04	0·01	0·005
75	76	4	,, 23	0·005	0·005	0·04	0·05	0·01	0·005
68	67	5	,, 25	0·005	0·005	0·06	0·05	0·005	0·005
68	69	6	,, 28	0·005	0·005	0·07	0·03	0·005	0·005
67	68	7	,, 30	0·005	0·005	0·06	0·03	0·005	0·005

Note.—No rain since October 18th.

10 a.m. and 4 to 5 p.m.; they were recorded because more rapid changes might be expected in warm than in cold weather.

I may remark that the determinations were made as recommended by Mr. Wanklyn, and that the sodium carbonate used for the free ammonia and the potash and potassium permanganate used for the albumenoid ammonia were boiled until they yielded distillates free from ammonia, and the distilled water used was also distilled from potash and potassium permanganate until free from ammonia.

(To be continued).

ACTION OF NITRIC ACID ON THE LIGNO-CELLULOSES.

By E. C. C. BALY and J. C. CHORLEY.

From the researches of Cross and Bevan, the results of which are summarised in a recent monograph ("Cellulose," Longmans, London, 1895), it is evident that the ligno-celluloses are not *mixtures* of cellulose and "incrusting substances," but ethereal compounds of cellulose with the complex of groups which may be conveniently included in the term "non-cellulose."

The interaction of the ligno-celluloses and dilute nitric acid which has been investigated by these chemists (*Berl. Ber.*, 1891, 1772; *Proc. Chem. Soc.*, xcvi., 61) has been shown to occur in the main between the acid and the latter complex, the cellulose being merely separated as an unaltered residue. The most prominent feature of the reaction is this sharp separation of the two groups of constituents; but the greater interest attaches to the elucidation of the complicated reactions by which the non-cellulose groups are entirely hydrolysed to soluble derivatives. This task we have undertaken: our investigations being devoted, in the main, to a quantitative account of the gaseous product. It had been previously established (*loc. cit.*):—1. That the most characteristic of their products are nitrous oxide and hydrocyanic acid, indicating as they do the direct union of nitrogen to carbon. 2. That the specific decomposition depends upon the presence of nitrous acid and is entirely arrested by the addition of urea. 3. That the destructive oxidation of the non-cellulose is limited to a very small proportion of its constituent groups, the reaction being completed with relatively small proportions of the acid at considerable dilutions (3 to 5 per cent HNO_3), and at low temperatures; further, the proportion of gaseous carbon compounds formed in the reaction is relatively small. 4. Lastly, that the proportion of N in combination with the non-cellulose groups, at any period of the decomposition is relatively small.

In our experiments we have taken beech wood as representing the class of fully lignified fibres; the proportion of nitric acid usually 33 per cent (HNO_3) of the weight of the wood in 10 per cent aqueous solution, and the conditions four to five hours heating in the water-bath, which takes the decomposition to the extreme limit, *i.e.*, with almost complete elimination of the N in the form of gaseous products.

The gaseous products of the decomposition being CO, CO_2, N_2O_4, N_2O, N_2, HCN, this separate estimation involved no small analytical difficulties.

The following are the actual details of the experiments:—

10 grms. of wood were placed in a flask together with 35 c.c. of 9·64 per cent HNO_3, immersed in a water-bath, and the products led through absorption vessels as follows:—

(*a*) Dilute sulphuric acid to which a standardised solution of potassium permanganate was added continuously in slight excess (estimation of N_2O_4+HCN jointly).* (*b*) The gas was then dried over calcium chloride, and passed through (*c*) weighed tubes containing soda-lime (estimation CO_2). (*d*) The remaining gases were collected over mercury and analysed by the following methods:—

1. N_2O_2, after adding O and absorption of N_2O_4.
2. CO. A known volume of H was added, and after explosion and absorption by KOH the CO was calculated from the total contraction. It was assumed that H and O combine by preference to the exclusion of the N_2O.
3. N_2O. A second explosion gave the data for calculating the proportion of this gas.
4. N_2 was calculated from the original gas.

Before commencing the whole of the apparatus was, as far as possible, exhausted of air.

In (*a*) the strength of the potassium permanganate solution was such that 1 c.c. was equivalent to 0·05 grm. NO_2. 25 c.c. of this were used, and the excess titrated with iron solution; this excess was 1·93 c.c., so that the solution used was 23·07 c.c., equivalent to 1·153 grms. NO_2, but which represents both the HCN and NO_2. In a collateral experiment the total HCN was estimated as AgCN and found to be 0·116 grm., which is equivalent to 0·395 grm. of NO_2, leaving 0·758 grm. NO_2 actually evolved (subject to a further correction which follows later). The CO_2 estimated by the increase of weight in the soda-lime tube (*c*) was 0·268 grm.

The gas in the gas-holder was 350 c.c. at 16° and 757 m.m., which was analysed as below.

The N_2O_2 was estimated by the contraction in volume resulting from the absorption of N_2O_4 formed on the addition of a known volume of O.

A known volume of H was then added and the gas mixture exploded. From the contraction in volume and absorption by KOH the CO was estimated; it was assumed that the H and O combined in preference to the H and N_2O. After further addition of H, the mixture was again exploded and the N_2O calculated.

From the volume of the residual gas the N could be calculated. In an actual experiment the following were the numbers obtained:—

	C.c.
Original volume of gas	5·67
Oxygen added	2·95
Volume after absorption by KOH	6·77
Hydrogen added..	0·95
Volume after explosion and KOH	5·45
Hydrogen added..	10·48
Volume after explosion	9·95

Calculation.—Contraction due to the absorption of NO_2=1·85 c.c.; this=1·23 c.c. of NO and 0·62 c.c. of O used (*a*). The contraction after the first explosion=2·27 c.c.; of this, 0·95+3÷2=1·42 is due to the H_2O; therefore contraction due to the CO_2=0·85 c.c.; this gives 0·56 c.c. of CO and 0·28 of O used (*b*). The O combining with the H being 0·47 c.c. The total O used is, therefore, 0·28+0·47+0·62=1·37 c.c. The O left is therefore 2·95 − 1·37 = 1·58 c.c. After the second explosion the total contraction was 5·98 c.c.; of this, 4·74 is due to the 1·58 c.c. of O left; therefore the contraction due to the N_2O=1·24 c.c. Now, the H added was 10·48 c.c.; of this, 3·16 c.c. was used by the O, and 1·24 c.c. by the N_2O. The total H used=1·24+3·16=4·40 c.c.; the H left was, therefore, 10·48−4·40=6·08 c.c. The N formed by the decomposition of the N_2O=1·24 c.c.; therefore the N originally present in the gas was 9·95−6·08−1·24=2·63 c.c.

	C.c.	Per cent.
N	2·63	46·36
N_2O	1·24	21·87
NO	1·23	21·69
CO	0·56	9·87
	5·66	99·79

---

* The HCN was separately estimated in independent experiments as AgCN (*infra*).

The N in this analysis is too high, owing to the presence of a small quantity of air originally present in the apparatus, in amount about 14 c.c., and, of course, being the first gas to enter the holder the numbers obtained must therefore be corrected as under.

	Per cent.
N .. .. —	=44·2
N_2O	=22·8
NO	=22·6
CO	=10·3
	99·9

In calculating the results to the original weight of interacting substances—wood and nitric acid—the gas remaining in the absorption vessels and flask had to be taken into account, and on the assumption of more or less uniform composition.

1. The volume of the soda-lime tubes (*c*) with connections .. .. = 30 c.c.
2. Between these and the surface of the $KMnO_4$ solution .. .. = 145 „
3. The volume of the flask less wood and acid .. .. = 400 „

The volume of the gases were measured at 16° and 767 m.m., except the gases in the reaction flask, which were at 95°. The gas having the composition of that analysed was 350+30 c.c. =380 c.c. from (1), and to this must be also added 144 c.c. CO_2, being that absorbed by the soda-lime. Between the soda-lime tube and the $KMnO_4$ solution there were 145 c.c. of gas (2) containing CO_2; this, by calculation, contains 40 c.c. CO_2, leaving 145 − 40 = 105 c.c. of analysed gas. The total CO_2 which passed the $KMnO_4$ = 144+40=184 c.c. So that a total of 669 (380+184+105) had passed through the $KMnO_4$. Now, 400 c.c. of gas was left in the flask at 160 m.m. and 95° =62 c.c. at 0° and 760 m.m. Between this 62 c.c. and the 669 c.c. the HCN must be proportionately divided, *i.e.*, 88 c.c. HCN have been absorbed by the $KMnO_4$ and 8 c.c. left in the flask; 88 c.c. HCN=0·364 grm. NO_2; therefore = 1·153−0·364=0·789 grm. is the true amount of NO_2 given off by the wood.

54 c.c. are left in the flask, which must contain 15 c.c. of CO_2, leaving 39 c.c. of gas as analysed.

Total analysed gas is, therefore, 380+105=485 c.c. at 16° and 757 m.m. + 39 c.c. at 0° and 760 m.m. =494 c.c. at 0° and 760 m.m., less 14 c.c. of N from air present =480 c.c. The total CO_2=184+15 c.c.=199 c.c. at 0° and 760 m.m.

	Results. C.c.	Per cent relation.	Weights. Grms.	Containing N. Grms.	Containing C.
N_2	212	18·3	0·266	0·266	
N_2O.. ..	109	9·4	0·215	0·137	
N_2O_2 ..	108	9·3	0·144	0·067	
N_2O_4 ..	383	33·2	0·789	0·240	
HCN ..	96	8·3	0·116	0·060	0·051
CO_2.. ..	199	17·2	0·393		0·107
CO	49	4·3	0·061		0·026
	1156	100·0	1·984	0·770	0·184

In regard to the accuracy of the results contained in the above Table: the CO_2, HCN, and N_2O_4, being estimated directly, the results may be taken as correct within the limits of the ordinary errors.

In calculating the remainder it was necessary, as stated, to make certain assumptions, to which larger errors attach. The degree of approximation may be estimated by taking the statistics of nitrogen: the N as HNO_3 taken was 0·750; the N calculated from the estimated volume of N and N compounds evolved is 0·770. Taking into account the unusual complications involved, and the purpose of this section of our observations, the results are sufficiently close to establish the main features of the decomposition.

First. The N_2O_4 and N_2O_2 representing 52·4 per cent of the N of the HNO_3 taken, it is evident that the proportion of nitric acid undergoing complete deoxidation is 20 per cent on the wood.

Second. The wood substance may be taken as containing approximately 50 per cent C. Of 4·5 grms. C., therefore, in 9 grms. wood, 0·133 is destructively oxidised to gaseous compounds—*i. e.*, only 2·95 per cent.

Before drawing final conclusions as to the mechanism of the reaction, we have to deal with the remaining products.

In the experiment described above the following were estimated :—

(*a*) *Fibrous Residue :* the ultimate fibres of the wood in the condition of approximately pure cellulose	48·00
(*b*) *Volatile Acid :* chiefly acetic, calculated as acetic	11·80
(*c*) *Oxalic Acid :* precipitated as Ca salt in acetic acid solution..	3·84
(*d*) *Soluble Derivatives of Non-cellulose :* ..	26·16
	89·80

(*a*). Of this "cellulose" residue little need be said. It contains oxycellulose groups, giving, on distillation with hydrochloric acid (1·06 sp. gr.), 4·5 per cent furfural. On treatment with nitrating acid a highly nitrated product was obtained. The following experiment, carried out comparatively with cotton, may be cited :—

	Yield p. c. in cellulose.	P. c. N in product.
Beech cellulose	170·4	12·91
Cotton	174·0	12·96

On treatment with HNO_3, of 45 sp. gr. alone—immersion for three minutes, followed by cold water :—

Yield of nitrate, 140·3 p.c. N p.c. in nitrate, 11·0.

(*b*). The *Volatile Acid.*—A large number of determinations of these products were made, the proportion of acid to wood being varied, and also the duration of the digestion. In cases where the soluble products contained NO residue, the solutions were treated with iron (wire) in presence of sulphuric acid, and distilled. The distillates, free from N acids, were titrated with normal soda solutions. The yields varied from 8 to 12 per cent, calculated as acetic acid. In some cases the solutions were oxidised with permanganate before distillation : the yields of volatile acid were, however, not increased.

Comparative experiments were also made with other typical ligno-celluloses. Jute, which has the same general features as beech-wood, gave similarly higher yields (12 per cent). Pine wood, on the other hand, representing a totally different type of lignification, gave low yields (3 to 4 per cent). These results agree with those obtained in destructive distillation.

(*c*). The *Oxalic Acid* is present in small proportion (3 to 4 per cent of the wood). Taken together with the CO_2 and CO, as representing jointly the products of destructive oxidation, the proportion of the ligno-cellulose undergoing this complete resolution may be taken at about 10 per cent.

(*d*). On evaporating the solution of the soluble by-products of the reaction, a yellow gummy residue is obtained—a mixture of ill-defined bodies of pronounced acid characteristics. All attempts to convert this complex into the well-defined dibasic acids—of the dimensions of C_6 or C_5—have failed. On further oxidation with nitric acid, under carefully regulated conditions, there is a considerable further formation of oxalic acid with volatile acids and oxides of carbon.

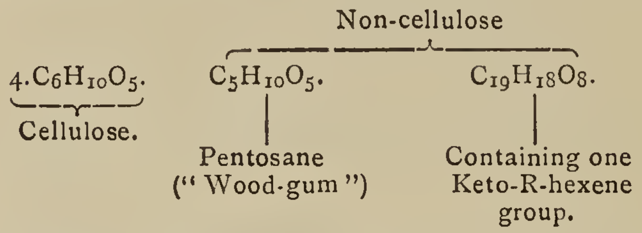
By fusion with the alkaline hydrates at 250°, the complex is resolved into carbonic, oxalic, and acetic acids. No aromatic products are formed.

As directly obtained in the original reaction, the products retain many of the essential characteristics of the non-cellulose constituents of the original wood—notably the property of condensation to furfural.

It appears, therefore, generally that in the original reaction the first groups to be attacked are the keto-R-hexene molecules of the ligno-cellulose: these ultimately undergo destructive oxidation. The more easily hydrolysable groups—*e.g.*, pentosans and β-celluloses—are next attacked, and are dissolved with more or less attendant oxidation, according to the duration of temperature of the reactions.

Without attempting an exact formulation of the reactions, the numerical relationships thus established may be summed up in approximate molecular ratios as follows:—

The ligno-cellulose may be regarded as—



$$\underbrace{4.C_6H_{10}O_5.}_{\text{Cellulose.}} \qquad \overbrace{C_5H_{10}O_5. \qquad C_{19}H_{18}O_8.}^{\text{Non-cellulose}}$$

Pentosane ("Wood-gum")

Containing one Keto-R-hexene group.

Taking into account only the HNO_3 deoxidised to N_2O+N_2, the molecular ratio is $6HNO_3$.

The reaction consists then, in the main, in the destructive oxidation of the one keto-hexene group of the non-cellulose complex; the acetic acid being formed partly from this group, with CH_3 residues obtained from groups in combination.

The nitric acid is broken down as below:—

$$12HNO_3=6H_2O+4N_2+2N_2O+14O_2.$$

Taking an approximate formula, $C_6H_6O_3$, for the hexene group, and allowing for the destructive oxidation of the C_6 nucleus, with the attendant union of COOH to CH_3, the molecular proportion of these characteristic products is—

$$2.C_2H_4O_2 : 4[CO_2,CO,C_2H_2O_4],$$

i.e., of the 6 carbons 2 are split off as acetic acid; the remainder are similarly oxidised, and after oxidation two are liberated in the simpler forms, and two remain in the residual solution.

The remaining groups of the complex ligno-cellulose formulated above are resolved as follows:—

The cellulose is separated insoluble in the approximate ratio* $4C_6H_{10}O_5$; the pentosan is dissolved, and the residues of the lignone complex also hydrolysed and dissolved.

Under the conditions of action described above the resolution is complete; the reaction may, on the other hand, be easily regulated to any desired limit, and the isolation of the cellulose completed by treatment with alkaline solutions.

The reactions, however, retain their specific characteristics through a wide range of variations of the conditions: in all cases it is the unsaturated groups, specially characteristic of the lignified celluloses, which are selectively and specifically attacked.

Laboratory of Messrs. Cross and Bevan,
London, W.C.

Laboratory Apparatus for Fractionated Distillations.—P. Monnet.—The apparatus cannot be described intelligibly without the accompanying full-page plate. The essential novelty is that the vapours are exposed to filings or fragments of metal. The author has used small shot (No. 6), though for very volatile liquids other sizes may be introduced, each kind separated from the others by means of copper gauze.—*Bull. de la Soc. Chim. de Paris*, xii.-xiv., No. 3.

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* The cellulose differs, it may be again noted, from the typical cellulose of this formula, containing only 43·0 per cent C., and yielding 4 to 5 per cent furfural on boiling with hydrochloric acid.

ON THE
PHOTOGRAPHY OF THE HIGHEST RAYS OF THE SPECTRUM.*

By VICTOR SCHUMANN, Leipzic.

"April 28th, 1895.

"At the commencement of this month I have, for the first time, photographed the spectrum of air far beyond the wave-length 180·0 Angström's scale, and have found that air, notwithstanding its untransmissiveness for the shortest wave-lengths, develops an astonishing energy. For instance, one of these photographs of the air, in a length of 34 m.m., shows more than fifty bands, all shading off towards the red. I have resolved many of these bands into lines.

"My present photographs of the hydrogen spectrum have shown a greater wealth of lines than might have been expected from my former estimate (600 lines). I have resolved the district situate beyond w.-l. 180·0 Angström's scale into seven districts, each of 3 degrees in extent. The first three regions contain 750 lines; one of them, with a length of 13 m.m., 350 lines. At present I estimate the total number of the lines of this district at 1500 to 2000."

THE REDUCTION OF ALUMINA CONSIDERED FROM A THERMO-CHEMICAL STANDPOINT.†

By JOSEPH W. RICHARDS, A.C., Ph.D.

The writer is a firm believer in the usefulnes of thermochemical data as a guide in chemical experiment. However, the deductions drawn from these data are often incorrect, because all the conditions have not been taken into account. Berthelot has postulated the "law of maximum work," which affirms that every chemical reaction takes place with the maximum production of heat possible by the combination of the reacting substances. This law, however, is too limited; it leaves out of consideration altogether the disturbing effect of the relative masses of the substances, their physical condition, and the physical condition of the products. For instance, an excess of a reducing agent is often necessary to reduce an oxide, producing or causing to take place a highly endothermic reaction. Again, if one of the possible products of a reaction would be in such a physical condition as to be quickly and completely removed from the sphere of the reacting bodies, its formation will be greatly accelerated. If two solutions are mixed, and one of the possible products of their reaction is insoluble in the solution, this fact will determine the formation of that substance, even though the reaction is an endothermic one. The heat deficit will simply be made up by an abstraction of heat from the solution; it will be cooled. Similarly, if two solids or liquids, or a solid and a liquid, are brought into intimate contact, and the possible result of their reaction should be a gas, the reaction will tend to take place, even if endothermic, because the gas escapes from the field of reaction as soon as produced, and so the inverse reaction is prevented. In such a case, putting pressure on the substances would hinder the formation of gas and retard the reaction; removing the pressure would facilitate the reaction. It has been proved, experimentally, that mercuric oxide and carbon react at a lower temperature when warmed in a vacuum than when at ordinary pressure.

Another important point is, that there is, under a given pressure, a critical point of temperature at which reactions first take place, the explanation of which is that the

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* Extract from a letter to Mr. Crookes.

† Read before the Chemical Section of the Franklin Institute, February 19, 1895.

particles of the original substances are themselves bound together by chemical affinity, and that the molecular vibration corresponding to a certain temperature is necessary before the new affinities tending to produce the reaction can overcome the original affinities of the primary substances. At 555° C. the atoms of oxygen and hydrogen, in the molecules of their respective gases, are vibrating to such distances from their mutual centre of attraction, that the new affinity of the unlike atoms for each other is able to disrupt the original molecules, and combination occurs. Similarly, carbonic oxide can break up the oxygen molecule only at 655° C. These remarks apply to the free gases at ordinary pressure. Under other conditions, the oxidation can go on at different temperatures.

If the substances are brought to the critical temperature at which they react, and the reaction at that temperature is exothermic, then the exchange will take place and proceed of itself until complete. If the reaction is endothermic, the first reacting portions absorb heat from the rest and lower the temperature below the critical point, thus putting a stop to the reaction, the exchange starts again only when the temperature is kept up to the critical point by the liberal supply of heat from without. This is the *modus operandi* of the reduction of many strong oxides.

The heat of formation of a molecular weight of alumina (102 parts) was determined by Baille and Féry, by oxidising aluminium amalgam. The reaction is—

$$Al_2Hg_3+3O=Al_2O_3+3Hg=+392,600 \text{ calories.}$$

This is evidently the heat of oxidation of liquid aluminium to solid alumina, *minus* the heat of formation of Al_2Hg_3. This latter quantity is unknown, but is probably quite small. These investigators determined the heat of hydration of alumina; thus—

$$Al_2O_3+3H_2O=2Al(OH)_3+3000 \text{ calories.}$$

Berthelot, long previously had found the heat of formation of hydrated alumina to be 391,600 calories. This would give 388,600 for anhydrous alumina, but this figure is based on the oxidation of solid aluminium. To compare it with Baille and Féry's figures, we must *add* to it the latent heat of aluminium at 0° C., which is calculated as follows:—

		Calories.
Latent heat of 1 kilo. aluminium at the melting point		100·0
Heat given out by 1 kilo. of molten aluminium in falling from 625° to 0°=625 ×0·308 (sp. heat molten aluminium), determined by Pionchon	Cal. 192·5	
Heat given out by 1 kilo. of solid aluminium through the same range (writer's experiments)	158·3	
Decrease in the latent heat		34·2
Latent heat of 1 kilo. at 0° C.		65·8
The latent heat of 54 kilos. (Al_2) is, therefore		3550·0

Adding this to Berthelot's corrected value for anhydrous alumina from solid aluminium, the sum is 292,150 calories. This agrees so closely with Baille and Féry's figures that the latter are accepted as being very near the truth.

Concerning the reduction of this compound to metallic aluminium, two ways are possible—the direct and the indirect. By the first I mean the use of an agent which is powerful enough to reduce it to metal at a single step; by the indirect is meant, first, reducing alumina to a more tractable aluminium compound, and then reducing the latter. Leaving electricity entirely out of consideration, there are but very few reducing agents which can decompose alumina directly, and they only at very high temperatures. Sodium does not act on it at any temperature, since sodium oxide is a far weaker compound than alumina.

$$3Na_2+3O=3Na_2O+299,280 \text{ calories.}$$

If the alumina, however, is converted into an oxygen-free aluminium salt, its affinities are then much weaker, while the reducing-power of sodium is relatively much greater.

Chlorine and carbon together decompose alumina,—

$$Al_2O_3+C+6Cl=2AlCl_3+3CO.$$

Heat absorbed—		
Decomposing alumina		392,600
Heat liberated—		
Aluminium chloride	325,510	
Carbonic oxide	88,200	
		413,710
Excess of heat		21,110

This reaction proceeds easily at a bright red heat; in fact, we not only have an exothermic reaction, but the products also are all gaseous, and as soon as the critical temperature at which the reaction begins is reached, the operation proceeds rapidly and completely.

The aluminium chloride is easily reduced by sodium, potassium, lithium, and magnesium, perhaps to a slight degree by manganese and zinc, which have about an equal affinity for chlorine. No other substances, organic or inorganic, besides these few rare alkaline and alkaline-earth metals, have a heat of combination with chlorine sufficient to decompose aluminium chloride.

Bromine and iodine vapours do not act like chlorine, and the reason is seen in casting up the thermal data. The difference between the heat of formation of alumina and 3 molecules of carbonic oxide is 392,600−88,200= 304,400 calories. Against this, chlorine formed aluminium chloride and gave 325,510 calories, making the reaction exothermic by 21,110 calories. Bromine, however, in forming the bromide, gives only 243,550 calories, leaving a deficit of 60,850 calories, while iodine gives only 144,310, leaving a deficit of 160,190 calories. The only known way of making these compounds is directly from aluminium itself.

Sulphur, also, is unable, either alone or with the assistance of carbon, to split up alumina. The heat of formation of aluminium sulphide being 127,950 (from liquid aluminium), the enormous deficit of 304,400 − 127,950= 176,450 calories, makes the reaction impracticable. However, when carbon bisulphide vapour is passed over white-hot alumina, aluminium sulphide is formed. It would appear at first sight as if the compound of carbon and sulphur would be less likely to produce the reaction than those elements uncombined; but the secret of this paradox is disclosed when we note that carbon bisulphide is one of the few endothermic compounds, absorbing 29,000 calories in its formation, and giving out just that amount in its decomposition. This helps to reduce the deficit by just so much. Further, carbonic oxide is not formed, but carbonyl sulphide, which has a heat of formation 4700 calories higher for each atom of oxygen taken up. Casting up the thermal data, we have—

$$Al_2O_3+3CS_2=Al_2S_3+3COS.$$

		Calories.
Heat absorbed—		
Decomposing alumina		392,600
Heat evolved—		
Formation of aluminium sulphide	127,950	
,, ,, carbonyl sulphide	102,300	
Decomposition of carbon bisulphide	87,000	
		317,250
Heat deficit		75,350

This is still a large deficiency, but the critical temperature for the reaction is a white heat, and, if the supply of carbon bisulphide is abundant, and the heating is kept up energetically, the reaction is practicable.

As for reducing this sulphide to metal, thermal data show us that only the alkaline and alkaline-earth metals can accomplish it easily, while manganese, zinc, tin, iron, and copper can do it to a small extent when used in large excess, making use of the influence of mass to bring about the endothermic reaction. This compound recommends itself more particularly for electrolytic decomposition. When mixed with an alkaline sulphide it forms an easily fusible double sulphide, which theoretically requires less than one volt to decompose it.

Alumina is easily converted into its fluoride, which, however, can only be decomposed chemically by the alkaline or alkaline-earth metals. Even fluorine alone acts energetically on it, raising it to incandescence.

The reaction—

$$Al_2O_3 + 6F = 2AlF_3 + 3O$$

sets free 555,550 − 392,600 = 162,950 calories, which accounts for the phenomena observed.

Even hydrofluoric acid gas can be used for the reaction, the splitting up of six molecules of gaseous hydrofluoric acid requiring, at 0° C., 222,600 calories, against which we have the formation of three molecules of water, 174,300 calories, leaving for the reaction a net excess of—

$$Al_2O_3 + 6HF = 2AlF_3 + 3H_2O + 114{,}650 \text{ calories.}$$

A reaction similar to this is impracticable with hydrochloric acid gas, and we find that it would be endothermic to the extent of about 30,000 calories.

Direct Reduction.

Minet has measured carefully the voltage required to decompose alumina dissolved in a fluoride bath, using a carbon anode, at which carbonic oxide is formed. As one volt represents a thermal value of 23,000 calories for each equivalent of oxygen liberated, it would represent 23,000 × 6 = 138,000 calories for each molecule of alumina split up. The number of calories represents, therefore, the thermal value of the following reaction:—

$$Al_2O_3 + 3C = Al_2 + 3CO$$

at the temperatures given. Minet's best experiments gave:—

Temperature.	Voltage.	Calorific equivalent (3O),
900°	2·40	331,000
1100°	2·17	299,460

If we can add to these numbers the heat evolved by the reaction $3C + 3O = 3CO$, at these temperatures, we shall obtain the value of the reaction $Al_2 + O_3$, or the heat of oxidation of liquid aluminium to liquid alumina. This calculation is made as follows:—

$$C + O = CO + 29{,}400 \text{ calories at } 0° \text{ (Berthelot).}$$

$$\text{Specific heat of carbon } (t > 900°)\ 0{\cdot}53 \times \frac{134{\cdot}6}{t} \qquad (a)$$

(Pionchon).

$$\text{Specific heat of oxygen} \ldots\ 0{\cdot}2114 + 0{\cdot}00001875\,t \qquad (b)$$

(Le Chatelier and Mallard).

$$\text{Specific heat of carbonic oxide} \ldots\ldots\ldots\ldots\ 0{\cdot}245 + 0{\cdot}0006\,t \qquad (c)$$

(Regnault).

Therefore,—

$$C + O\left(\begin{matrix}\text{at } t° \\ t > 900°\end{matrix}\right) = 29{,}400 + (12a + 16b - 28c)\,t.$$
$$= 27{,}785 + 2{\cdot}8824\,t - 0{\cdot}0003\,t^2.$$

Substituting, we have—

At 900°, $C + O = 30{,}136$ $3(C + O) = 99{,}408$
At 1100°, $C + O = 30{,}592$ $3(C + O) = 91{,}776$

Adding these to the values of the reaction given by Minet's experiments, we have—

At 900°, $Al_2 + O_3 = 331{,}000 + 90{,}408 = 421{,}408$ cal.
At 1100°, $Al_2 + O_3 = 299{,}460 + 91{,}776 = 391{,}236$ cal.

Now, we know that at 0°, $Al_2 + O_3 = 391{,}600$ calories, the only difference between this and the figures just derived being that the latter is calculated for *solid* alumina. For liquid alumina, we should have to subtract from it the latent heat of fusion of alumina. This is not known, but if we estimate it at 43 calories per kilo. (from analogy with other oxides), we may subtract 43 × 102 = 4400 calories. We then have the heat of formation of liquid alumina from liquid aluminium, as follows:—

	Calories.
0°	387,200
900°	421,408
1100°	391,236

It will be noticed that the value has reached a maximum between 0° and 900°, and is rapidly decreasing; in other words, above 1000° alumina rapidly becomes easier to decompose. A curve passing through the above values would be of the following form:—

$$Q = 387{,}200 + 192{\cdot}6\,t - 0{\cdot}1716\,t^2.$$

The question now is—At what temperature would the heat of oxidation of our reducing agents equal the heat of formation of alumina? We may fairly assume that if that point is above the critical point for the reaction, reduction will there begin.

Carbon.—The formula for the heat of oxidation of carbon to carbonic oxide has already been deduced. We therefore have—

$$Al_2 + O_3 = 387{,}200 + 192{\cdot}6\,t - 0{\cdot}1716\,t^2$$
$$3(C + O) = 83{,}355 + 8{\cdot}6472\,t - 0{\cdot}0009\,t^2$$

When these two expressions become equal to each other,

$$t = 1980°.$$

If liquid carbon is the reducing agent, its efficacy is about 21,000 calories greater than solid carbon, and—

$$t = 1940°.$$

As verifying these calculations, I may refer to the fact that liquid alumina is, beyond a doubt, reduced by carbon in electric furnaces, because the output of aluminium is greater than the number of ampères passing through the furnace could theoretically produce, and, also, because decomposition can be produced by a rapidly-alternating current, where electrolysis is out of question. The temperature in such furnaces is probably about 3000°. Again, in a Pennsylvania iron blast-furnace, in which the temperature is almost certainly not over 2000°, as much as 1 per cent of aluminium has been reduced into the iron. The liquid carbon in the iron in the crucible is here the reducing agent, reducing aluminium from a slag carrying as high as 25 per cent of alumina.

It thus appears that both calculation and practice unite in showing that carbon begins to reduce alumina in the neighbourhood of 2000° C.

Hydrogen.—

$$H_2 + O = 69{,}000 \text{ calories (to liquid } H_2O \text{ at } 0°)$$
$$= 58{,}100 \quad ,, \quad \text{(to vapour of water at } 0°)$$
$$\text{Specific heat of hydrogen} = 3{\cdot}3820 + 0{\cdot}0003\,t \qquad (a)$$
$$,, \quad ,, \quad \text{oxygen} = 0{\cdot}2114 + 0{\cdot}00001875\,t \qquad (b)$$
$$,, \quad ,, \quad \text{water vapour} = 0{\cdot}4208 + 0{\cdot}000182\,t \qquad (c)$$
$$H_2 + O\ (\text{at } t°) = 58{,}100 + (2a + 16b - 18c)t$$
$$= 58{,}100 + 2{\cdot}572\,t - 0{\cdot}0024\,t^2.$$

We therefore have:—

$$Al_2 + O_3 = 387{,}200 + 192{\cdot}6\,t - 0{\cdot}1716\,t^2$$
$$3(H_2 + O) = 174{,}300 + 7{\cdot}716\,t - 0{\cdot}0072\,t^2$$

When these two expressions become equal to each other,

$$t = 1790°.$$

This is just about the melting-point of platinum, and may appear lower than can possibly be the fact; nevertheless, Mr. H. Warren, in England, has recently succeeded in reducing alumina to aluminium in a current of hydrogen gas, the alumina being inside a lime tube heated on the outside by the oxy-hydrogen flame. It is hardly possible that the temperature inside the tube could have exceeded 2000°, yet complete reduction to metallic globules was obtained.

This second confirmation of the calculations by experiment induces me to add, in conclusion, the following observations:—

Acetylene gas, C_2H_2, has a negative heat of formation of 51,500 calories. It is, therefore, just by that much a more powerful reducing agent than C_2 and H_2 alone. The equation is—

$$Al_2O_3 + C_2H_2 = Al_2 + 2CO + H_2O.$$

The thermal equations are—

$$\begin{array}{rcll} \underline{Al_2 + O_3} & \underline{=} & \underline{387{,}200 + 196{\cdot}2\,t - 0{\cdot}1716\,t^2} & (a) \\ 2(C + O) & = & 55{,}570 + 5{\cdot}7648\,t - 0{\cdot}0005\,t^2 & (b) \\ H_2 + O & = & 58{,}100 + 2{\cdot}572\,t - 0{\cdot}0024\,t^2 & (c) \\ C_2 - H_2 & = & 51{,}500 & (d) \end{array}$$

making $b + c + d = a$.

$$t = 1870°.$$

I am inclined to think that this highly endothermic compound would reduce alumina at an even lower temperature than this, because we have not only the benefit of its great heat of decomposition, but we also have, at the moment when it decomposes, the carbon and hydrogen atoms *in statu nascendi*, and we thus have all the advantages of a *nascent* reducing agent. I need not, to an audience of chemists, expatiate on the greater chemical activity of a nascent reducing agent.

The recent developments in the manufacture of calcium carbide and acetylene open up a possibility in the way of reducing alumina which may bear fruit. Allow me, at least, to claim for thermo-chemistry, rightly understood, that it is a most helpful guide to intelligent experiment.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

THE Exhibition of Scientific Apparatus and Processes at the Conversazione of the Royal Society, on Wednesday, May 1st, included some objects of exceptional interest.

Prof. Roberts-Austen, C.B., F.R.S., exhibited an electrical furnace used for fusing chromium, titanium, and other refractory metals. It consists of a fire-clay case lined with magnesia, and containing a magnesia crucible. The carbon poles are horizontal, and the arc is bent down upon the object to be heated by means of a magnet. For purposes of exhibition, an image of the molten contents of the crucible is projected upon a screen by means of a mirror and lens. The current is about 60 to 70 ampères at 100 volts.

The world-famed metallurgists, Messrs. Johnson, Matthey, and Co., exhibit a nugget of platinum, 158 ozs.; an ingot of palladium, of 1000 ozs.; a rhodium ingot, of 72 ozs.; osmium, both molten and as a sponge; ruthenium, fused by the arc; and pure iridium, in a rolled sheet.

Prof. Ramsay exhibited the spectra of argon, and of helium mixed with argon. There were shown spectra of argon obtained from air, and those of a mixture of argon and helium as extracted from the mineral clèveite. The sodium flame was shown to demonstrate the non-identity of the D_3 line of helium with the D_1 and D_2 lines of sodium.

Sir B. W. Richardson exhibited an electrical cabinet for hospital service, thus proving that medical electricity is not the exclusive property of the quacks.

The Cambridge Scientific Instrument Company displayed an improved type of spectrometer freed from certain inaccuracies.

The Marine Biological Association exhibited dilute formic aldehyd used for the preservation of transparent organisms, a new method of fixing methylen-blue preparations, as devised by Prof. Bath, of Berlin.

Mr. Francis Galton, F.R.S., &c., displayed enlarged finger-prints, serving for identifying suspected criminals.

Prof. V. B. Lewes exhibited the preparation of acetylene from calcium carbide, and its combustion for illuminating purposes.

Major Cardew exhibited specimens which have of late been the subject of discussion in connection with street-explosions. The deposits shown contained metallic sodium and potassium liberated electrolytically.

A most interesting exhibit by W. T. Burgess proves the reality of the transmission of infection, *i. e.*, of pathogenic microbia, by flies.

Prof. Gotch, F.R.S., and Dr. H. O. Forbes exhibited a living specimen of the *Malapterurus electricus*, from the River Senegal.

Prof. A. Liversidge, F.R.S., of Sydney, exhibited gold nuggets, etched so as to show their crystalline structure. The designs obtained closely resembled the well-known Widmanstatt figures as shown by most metallic meteorites.

PHYSICAL SOCIETY.

Ordinary Meeting, April 26th, 1895.

Mr. WALTER BAILY, Vice-President, in the Chair.

PROF. S. P. THOMPSON read a note on "*A Neglected Experiment of Ampère.*"

Ampère, in 1822, made an experiment which, if it had been properly followed up, must have led to the discovery of the induction of electric currents nearly ten years before the publication of Faraday's results. While attempting to discover the presence of an electric current in a conductor placed in the neighbourhood of another conductor in which an electric current was flowing, Ampère made the following experiment:—A coil of insulated copper strip was fixed with its plane vertical, and a copper ring was suspended by a fine metal wire so as to be concentric with the coil and to lie in the same plane. A bar magnet was so placed that if an electric current was induced in the suspended ring a deflection would be produced. No such deflection, however, was observed.

In 1822, in conjunction with De la Rive, Ampère repeated this experiment, using, in place of the bar magnet, a powerful horse-shoe magnet. He describes the result in the following words:—"The closed circuit under the influence of the current in the coil, but without any connection with this latter, was attracted and repelled alternately by the magnet, and this experiment would, consequently, leave no doubt as to the production of currents of electricity by induction if one had not suspected the presence of a small quantity of iron in the copper of which the ring was formed." This closing remark shows that they were looking for a permanent deflection. When, however, Faraday's results were published in 1831, Ampère, after again describing the experiment made in 1822 by himself and De la Rive, says:—"As soon as we connected a battery to the terminals of the conductor, the ring was attracted or repelled by the magnet, according to the pole that was within the ring, which showed the existence of an electric current produced by the influence of the current in the conducting wire.

Verdet, when describing the above experiment, falls into a curious error. He says the apparatus consisted of a ring of fine copper wire, suspended by a silk thread in front of the pole of an electro-magnet, in such a way that the plane of the ring was parallel to the plane of the turns of wire on the electro-magnet. On "making" the current the ring is said to have been repelled, but this deviation did not persist; and on "breaking" the current the ring was attracted, also only momentarily.

Mr. BLAKESLEY did not feel quite confident that in Verdet's form of the experiment there could ever be attraction. He also pointed out that, with an alternating current, the disc would tend to set itself parallel to the lines of force of the electro-magnet. With reference to repulsion by alternating currents, in one of Elihu Thompson's experiments, where a sphere is supported over an alternating pole, a screen being placed so as to partly shield this sphere, there is generally a misstatement as to the direction in which the sphere rotates. It rotates in such a direction that the part of the surface next the magnet moves towards the edge of the screen.

Dr. Burton said that, from the fact that when the current in the electro-magnet in Verdet's experiment is broken the induced current in the ring is in the same direction as the current in the magnet, the ring will be attracted.

Mr. Boys confirmed Dr. Burton's statement. He recommended setting the ring at an angle of 45° to the lines of force, under which circumstances a rotation would be obtained. A distinction must, he pointed out, be drawn between such an experiment as that of Verdet and those of Elihu Thompson. The repulsions observed in these latter were only due to the "lag" in the induced currents caused by self-induction. The best materials to use for all such experiments were magnesium and aluminium, since for a given mass these had the highest conductivity.

Mr. W. G. Rhodes read a paper entitled "*A Theory of the Synchronous Motor.*"

The object of this paper is to give as simple a treatment as possible of the mathematical part of the subject, and to give theoretical proofs of some experimental facts. Starting from the energy equation,—

$$p + c^2R = CE \cos \psi,$$

where p is the output of the motor, R the resistance of the armature, c the current through the armature, E the E.M.F. applied to the motor terminals, and ψ the phase difference between c and E, the cases of maximum output, zero output, minimum current at zero power, and maximum phase difference between c and E are considered. These results are, for the most part, obtained directly from the energy equation. The latter part of the paper is devoted to a discussion of the phase relationships between the current and the E.M.F.'s in a plant consisting of a generator and motor, and to the variations in the armature reactions in both generator and motor. A theoretical proof is given of the fact, observed by Prof. Silvanus Thompson and others, that an over-excited synchronous motor acts as a condenser, and tends to make the current lead before the generator's E.M.F.

Prof. S. P. Thompson said that the mathematical part of the paper was much simpler than that in previous investigations on this subject, and the method of arriving at the results by rejecting imaginary roots of the equations was particularly neat and instructive. The part of the paper relating to armature reactions and phase relationships was quite new. Two results deserved special attention; first, that the maximum current of zero power was the same as if the circuit was non-inductive; second, that the maximum current at zero power was double the current corresponding to maximum output.

Mr. Blakesley said that the paper did not consider the stability of the system, and he thought some of the results corresponded to regions of unstability.

A paper by Mr. Bryan, "*On a Simple Graphical Interpretation of the Determinantal Relation of Dynamics,*" was, in the absence of the author, read by Dr. Burton.

The relation is worked out for two specially simple systems possessing one degree of freedom: (1) a particle moving in a straight line with uniform acceleration; (2) a particle moving to and fro along a straight line with an acceleration directed towards a fixed point on the line, and proportional to the distance from that point (simple harmonic motion). On constructing a diagram in which the abscissæ represent values of the single coordinate of the particle, and the ordinates corresponding values of the momentum, the determinantal relation becomes equivalent to the constancy of the area of a certain elementary parallelogram. In case (1) this parallelogram moves along a parabola, experiencing a shear as it goes; while in case (2) there is no distortion, the (rectangular) parallelogram revolving about the origin of the diagram as if rigidly attached to an inextensible radius vector.

NOTICES OF BOOKS.

Addresses in Commemoration of Josiah Parsons Cooke, LL.D., Late President of the American Academy of Arts and Sciences. Delivered at the Meeting of the Academy December 12th, 1894. (Extracted from the *Proceedings*, vol. xxx.). Cambridge (U.S.A.): J. Wilson and Son, University Press.

A considerable part of this pamphlet is worthily taken up with a biographical notice of the deceased, who will be endeared to all true followers of Science by the successful energy with which, in addition to his valuable researches in professional duties, he fought for the recognition of chemistry as a subject not less valuable than the "humanities" intrenched behind centuries of tradition. Chemical teaching at Harvard College had become extinct, and Cooke had to re-establish it. It is remarked that, like Liebig, "he had neither taste nor aptitude for the dead languages, and it was only with much difficulty that he surmounted the barrier of Greek and Latin which guarded the approach to Harvard College."

This is additional evidence—if any such is still needed—how little proficiency in "classics" can be regarded as a gauge for the intellectual power of a youth. It took Cooke "seven years of hard fighting to get chemistry adopted by the College as anything but an extra." He had by degrees to eliminate "recitations"—we presume committing a text-book to memory—in favour of the laboratory method devised by Liebig and taken up by Wœhler. It is remarked, drily, that neither of Cooke's earlier books ("Chemical Physics" and "Chemical Physiology") was popular with the students. They could not be, as they obliged their readers to think, and there is no occupation more distasteful to an undergraduate.

As an instance of the imperfect equipment of the institutions of higher education, we learn that "there was neither gas nor running water in University Hall, and Mr. Cooke's nearest neighbour, on the adjoining corner of the basement, was a baker's oven, where considerable batches of bread were baked every morning and evening, and yeast was sold every afternoon. A pump in the cellar yielded water for both bakery and laboratory, and within 50 feet of the pump was a privy which served for the whole college! Surely any comment on such a state of things could only be an anti-climax. It was a very fortunate circumstance that Prof. Cooke had inherited wealth, and was consequently not brought to a stand-still by the parsimonious conduct of the governing body of the College. He often supplied the laboratory of the lecture-room, at his own expense, with costly pieces of apparatus. Nor was he exposed to the painful necessity of spending his time on analytical or consultation work. A characteristic feature in his conduct was the readiness with which he appreciated and took up any new discovery. He devised improvements in the spectroscope, and constructed the most powerful instrument of his day. Several of his papers owe their origin to his work in spectrum analysis. He made a careful and enthusiastic study of the radiometer, which he regarded as a fresh evidence of the existence of a molecular universe. He was a zealous and successful photographer.

Prof. Cooke deserves, in short, the utmost honour as a man who would not endure the attempts of the "poor humanist" to relegate Science to a position of inferiority, and to force "longs and shorts and gerund-grinding" upon minds who crave for a different pabulum. At the same time he regarded Science as an essential element in a truly liberal culture, and was free from the narrow utilitarianism which so many persons confound with or prefer to the quest of truth for its own sake.

Qualitative Chemical Analysis of Inorganic Substances, as Practised in Georgetown College, D.C. By Rev. H. T. B. Tarr and Rev. J. W. Fox. New York, Cincinnati, and Chicago: American Book Company.

This book, being chiefly based upon the recognised text-books of Fresenius and Watts, may be expected to prove trustworthy, as in fact it really is. The only point on which we should beg to differ from the authors is in the composition of magnesia mixture.

The authors use magnesium sulphate, which we find less satisfactory than the corresponding chloride. But, as a general principle, we dislike any analytical manual which omits the rarer elements. Such substances may at any time occur in natural minerals, or in artificial compounds and mixtures, and may modify the reactions which the student has been taught to expect. It is possible that in America the chemical public has not yet been so supersaturated with manuals, " manualettes," and handbooks, as has been the case in Britain.

We find here no reference to any syllabus, or to any examination for which the student has to prepare. This is a point which deserves our thankful acknowledgment.

The Pharmaceutical Journal of Australasia. Vol. viii., No. 2.

This Journal is less—much less—a scientific than a trade organ. There is an account of the position and prospects of Fremantle, and of Western Australia in general, not calculated to attract pharmacists or indeed settlers of any kind. Quacks, calling themselves " specialists," seem to be watchful and alert in the Colonies, and will need careful looking after.

The New Zealand Colonial Government has offered a prize of £1000 for the first 200 tons of crude potassium cyanide manufactured from local produce. Nitrogenous refuse suitable for this manufacture ought to be abundant, but we fear the Colonies—or indeed the entire Empire—will not supply the potash. But has a sufficient search been made?

We are happy to learn that the cultivation of perfume plants is being pushed forward at Dunelly. The temperature in South Australia (indoors) ranges from 90° to 98°,—a set-off, we presume, to the arctic weather with which the home-kingdoms have been afflicted.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 16, April 22, 1895.

New Deposit of Uranium.—Baron Nordenskiold.—I have not yet completed my researches on the uraniferous minerals. I believe I have this winter discovered a very important deposit of uranium. It is certain sedimentary beds of a carboniferous composition the ash of which yields from 2 to 3 per cent of uranium. This uraniferous substance contains also some nickel and rare earths and a considerable quantity of nitrogen. Perhaps it may also contain an abundant source of argon or of helium.—(*Extract from a letter from Baron Nordenskiold to M. Daubrée.*

Crystals Forming at the Bottom of a Solution Heavier than Themselves.—Lecoq de Boisbaudran.—On p. 539 of the present volume the author has described crystals forming on the surface of liquids lighter than themselves. He now has observed an inverse phenomenon in the case of sodium sulphate with 10 per cent Aq. He takes a solution of sodium iodide, saturated with sodium sulphate, and of a density a little greater than that of the crystals of sodium sulphate with 10 Aq. The crystals at first float upon the surface, but after a few days subside to the bottom.

Specific Heat and Boiling-point of Carbon.—J. Violle.—Above 1000° the mean specific heat of graphite increases in a linear manner with the temperature according to the formula—

$$C_o^t = 0{\cdot}355 + 0{\cdot}00006\,t.$$

The temperature of ebullition of carbon is 3600°.

On Photography in Natural Colours by the Indirect Method.—Aug. and Louis Lumière.—The authors obtain successively on the same plate three monochromes, red, yellow, and blue, from three corresponding negatives, using the precaution to isolate each image from the foregoing by an impenetrable layer, *e.g.*, collodion.

Molecular Rotation and Molecular Deviation.—Ph. A. Guye.—The author remarks that there are two manners of conceiving the mean deviation due to the action of an active molecule: the molecular rotation which supposes all the liquids brought to the same volume containing the same number of molecules and examined with the planimeter is one and the same thickness; the molecular deviation when we suppose all the active liquids examined with the polarimeter in depths such that the polarised ray always meets in its course the same number of active molecules in the direction of the length of the active medium.

Certain Derivatives of Quinone-di-ortho-amino-benzoic Acid.—J. Ville and Ch. Astre.—The action of reducing agents and of benzoyl chloride upon the above acid reveals in this compound the persistence of the quinonic function. On the other hand, the researches of Knapp on the chloroquinones (*Berichte*, xiv., p. 1233) show that the products obtained with the primary amines must be considered as derived from the quinones by the substitution of two groups (NHR')' for two hydrogens.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 108.

This number contains no chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 3, 1895.

At the meeting on January 11 the financial report of the Society for the past year was presented. It was accepted by acclamation, and a silver medal, bearing the likeness of Lavoisier, was voted to the retiring President, A. Scheurer-Kestner.

The staff and Council for the present year will be:—
President—Maquenne.
Vice-Presidents—Moissan, Wyrouboff, Béchamp, and Suilliot.
Secretaries—Béhal and Verneuil.
Vice-Secretariees—Bigot and Lindet.
Treasurer—Petit.
Achivarian—Cloëz.
Other Members of Council—Le Bel, André, Tanret, Riban, Friedel, Schützenberger, A. Combes, Hanriot, Scheurer-Kestner, Engel, Adrian, and Joly.

The non-resident members of Council are Péchiney, Buisine, Haller, and Barbier.

The President announced that he had received official information that the Congress of learned societies will be held at the Sorbonne, on April 16, at 2 p.m.

During the month of December, 1894, the Society took charge of three "sealed papers."

Project of Nomenclature of some Stereo-Chemical Isomers.—R. Lespieau.—The author's proposal cannot be explained without the insertion of a number of formulæ which are, in fact, diagrams.

On the Acid Potassium and Silver Fluorides.—M. Guntz.—A thermo-chemical paper. The author determines the formation-heats of the acid fluorides discovered by Moissan.

Certain Thiohypophosphates.—L. Ferrand.—The author has obtained and determined the thiohypophosphates of zinc, $P_2S_6Zn_2$, the corresponding cadmium salt, $P_2S_6Cd_2$, and the nickel salt, $P_2S_6Ni_2$.

Action of Chlorine upon the Secondary Alcohols.—A. Brochet.—The action of chlorine upon the secondary alcohols of the form $R.CHOH.CH_3$ gives chloro-acetones of the form $R.CO.C'Cl_3$.

Certain Glycerins derived from the Secondary Allylic Alcohols.—H. Fournier.—An examination of the glycerin of ethylallylcarbinol, of its triacetine, of the glycerin of isopropylallylcarbinol triacetine, of the glycerin of isobutylallylcarbinol, and that of phenylallylcarbinol.

Nitrosopropylacetamide.—F. Chancel.—This substance is mobile, of a rose colour if seen in a thick stratum, but yellow in slender layers, as is its aqueous solution. Its sp. gr. at 15° is near that of water, 1·035.

Presence of Glyoxylic Acid in Green Fruits.—H. Brunner and E. Chuard.—The authors reject the view of Ordonneau that the acid in question is the tartaro-malic. They have also recognised the presence of formic acid along with the glyoxylic and glycolic acids.

Researches on the Constitution of Hexamethyleneamine.—M. Delépine.

Hydrogenation of Hexamethyleneamine. Formation of Trimethylamine.—M. Delépine.—This paper, like the foregoing, does not admit of useful abstraction.

Essence of Cananga.—A. Reychler.—In a general manner the qualitative resemblance of the oil of ylang-ylang and that of cananga is so complete that it cannot be accidental. It is possible that the two essences are obtained from the same vegetable species.

Detection and Separation of Free Hydrochloric Acid and of Chlorides. Application to the Analysis of the Gastric Juice.—H. Lescoeur.—This paper will be inserted at some length.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Society of Arts, 8. (Cantor Lectures). "Recent American Methods and Appliances employed in the Metallurgy of Copper, Lead, Gold, and Silver," by James Douglas.
— Medical, 8. (General Meeting).
TUESDAY, 14th.—Royal Institution, 3. "Thirty Years' Progress in Biological Science," by Prof. E. Ray Lankester, F.R.S.
— Institute of Civil Engineers, 8.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
WEDNESDAY, 15th.—Society of Arts, 8. "Means for Mitigating the Fading of Pigments," by Captain W. de W. Abney, F.R.S.
— Microscopical, 8.
— Meteorological, 7.30.
THURSDAY, 16th.—Royal, 4 30.
— Royal Institution, 3. "The Liquefaction of Gases," by Prof. Dewar, F.R.S.
— Chemical, 8. Ballot for the Election of Fellows. "Kjeldahl's Process for the Determination of Nitrogen," by Dr. Bernard Dyer. "The Action of Nitrous Acid on 1 : 4 : 2 Dibromaniline," by Prof. Meldola, F.R.S., and E. R. Andrews. "Derivatives of Succinyl and Phthalyl Dithiocarbimides," by Prof. Dixon and Dr. Doran.
FRIDAY, 17th.—Royal Institution, 9. "Robert Louis Stevenson," by Prof. Walter Raleigh.
— Quekett Club, 8.
SATURDAY, 18th.—Royal Institution, 3. "Picture Making," by Seymour Lucas, A.R.A.

THE CHEMICAL NEWS.

VOL. LXXI., No. 1851.

THE POSITION OF ARGON IN THE PERIODIC SYSTEM.

By W. W. ANDREWS.

I HAVE been engaged in projecting the curves of atomic volume, melting-point, &c., into the vacant space between hydrogen and lithium, to see if, with corrected values, the Periodic Law can be made the instrument for prophecy, as in the cases of Sc, Ge, and Ga. The regularities of the curves show this, that the members of the second and third families, supra-beryllium and supra-boron, should have properties similar to argon, the former especially.

In the lower series, the neutral element is found in the fifth and sixth families, in the third between Al and Si, in the second at boron, and in the first it should be at supra-beryllium.

Not only so, the atomic volume curve should descend from H as it does from Li, Na, K, Rb, &c., and should rise at supra-nitrogen and supra-oxygen. If we take the value obtained from its alloys the atomic volume of H is

$$\frac{1}{0{\cdot}63} = 1{\cdot}587\,;$$

supra-Be should then be less than unity. The atomic weight of an element for that position should be about 1·5 or 1·6, and the density of argon is 1·5, perhaps 1·7 or 1·8 as a solid; these values give a value for atomic volume of the required dimensions.

But small atomic volume is the condition of polymerisation, or, rather, both spring from some common condition, great inter-atomic attractions. Great chemical inertness accompanies both of these. We may expect from the very small atomic volume less than unity, great attraction of supra-beryllium atoms for like atoms, and therefore little susceptibility to attack from other elements, and as the atomic volume is less than unity, several atoms would be crowded into the same *atomic* space—a new condition in gas chemistry. Would a polymerisation of a grade represented by the fraction—

$$\frac{40}{1{\cdot}5} = \frac{\text{seeming atomic weight of A}}{\text{atomic weight of supra-Be}} = 28$$

or thereabouts be too much to expect? Would not such a group of atoms act like single atoms, or the ordinary elementary molecules? Should it not also be expected to act like a perfectly round body, and therefore give the ratios between the specific heats exhibited by argon? Its spectrum should be like those found at the alkaline end of Lothar Meyer's table, and such I see is the case.

The melting point curve should rise rapidly from hydrogen to supra-carbon. Hydrogen should solidify at $-243+x$, perhaps -250 or -260. Argon, then, drops in the place of supra-Be in this curve also.

I am anxious to know its refraction-equivalent, and will wait with interest future developments. Berthelot, I see, reports an alkaline reaction from the new argon compound.

If the next few months bring the requisite facts, I shall have all my curves accurately drawn in a form ready for publication. The curves of atomic volume, melting points, of acid and alkaline power, if projected from Cs, Ba, La, and Ce over the vacant space to Os, Ir, Pt, Au, &c., and again over vacancy to Th and U, are such that these elements drop into their places in the three curves, and thus the whole is found to be one system. We ought to be able to prolong the curves into Series I. to hydrogen, though on account of the tendency to greater accentuation of difference, the task is one of greater difficulty.

Let us imitate the sublime faith of Mendeleeff, and we may rest assured that the order and multiplied analogies revealed by the Periodic Classification form a basis of fact which is not to be shaken. Argon and helium will drop into their places and open up new vistas of analogy and suggestion.

Science Laboratory, Mt. Allison University,
Sackville, N.B., Canada, April 29, 1895.

VOLUMETRIC DETERMINATION OF SUGAR BY AMMONIO-CUPRIC SOLUTION.*

By ZDENEK PESKA.

OF the various methods propounded for the quantitative determination of sugars, three have found favour in the eyes of chemists—the original Fehling titration, the improved Soxhlet process, and the Soxhlet-Allihn gravimetric method. The latter is most frequently employed, but occasionally, when speed is more important than minute accuracy, the old Fehling process is still used.

The gravimetric method is, however, not always free from serious faults. For instance, personal experience has shown that various kinds of asbestos are not unaffected by the alkaline-copper solution, the filter itself losing weight, according as the operation is performed rapidly or slowly. Hence the only method which can lay claim to accuracy is the Soxhlet titration, but this unfortunately requires such a long time for its performance that it is seldom used, and is also open to objection in that where ammonia compounds are present in the sugar solution some of the cuprous oxide dissolves, and a copper reaction may be detected in the filtrate. This circumstance may, however, be utilised in quantitative estimations of sugar. If an excess of ammonia be added to the Fehling solution the cuprous oxide remains dissolved, the deep blue liquid containing ammonio-cupric salts being reduced, by a sufficient quantity of sugar, to a colourless solution of ammonio-cuprous compounds.

This idea was utilised by Pavy (CHEMICAL NEWS, xxxix., 77), who added a large excess of ammonia to the Fehling solution and treated the boiling liquid with sugar solution until decolouration was effected. Ammonia was evolved on boiling, and Pavy relied on this to ensure the exclusion of air necessary to prevent the re-oxidation of the cuprous solution. It will be readily understood that this procedure can only effect an incomplete exclusion of air, and that the proportion of alkali in the solution—which influences the reducing power of the sugars—does not remain constant when the liquid is boiled.

Attempts made to totally exclude the air by means of a gentle current of hydrogen passing through the reacting liquid in a flask did not succeed. In the first place, the removal of the final traces of air from the generating flask and washing apparatus was very tedious; and, secondly, the hydrogen carried away a portion of the ammonia from the solution, thus perpetuating the second error previously referred to.

However, by employing, instead of an indifferent gas, an inert liquid of lower specific gravity than the solution, the work can be carried out satisfactorily, and for this purpose *pure paraffin oil* is particularly suitable. If the Fehling solution mixed with ammonia be covered with a layer of about 0·5 c.m. of paraffin oil, not only is contact with air cut off, but the escape of ammonia is prevented, and constancy in the proportions of the solution ensured.

The added ammonia must be sufficient in quantity to maintain the cuprous oxide in solution, but not so large

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* "Vorlaüfige Mittheilung aus den Abhandlungen der böhmischen Akademie der Wissenschaften" (through *Zeitschrift fur Rübenzucker-Industrie*, xxxiv., pp. 165—168).

as prescribed by Pavy, as an evolution of the gas will occur when heat is applied, which, by disturbing the oil layer, will facilitate the admission of air. The proportion experimentally ascertained as most suitable is 80 c.c. of 25 per cent liquid ammonia per 3·634 grms. of cupric sulphate; the reaction should not be carried out at boiling heat, but at lower temperature (80° to 85° C.).

At first ammonio-cupric solution was used equal to decinormal Fehling, but it being found that only very small amounts of sugar could be treated by this strength (a maximum of 0·044 grm. of glycose per 100 c.c. of copper solution), a solution twice as strong as the above was prepared and found satisfactory. A higher degree of concentration is not recommended on account of the large amount of ammonia requisite.

The solution employed is made up in two stages, as follows:—Dissolve 6·927 grms. of crystallised cupric sulphate in water, adding 160 c.c. of 25 per cent ammonia, and make up to 500 c.c. on cooling. Then dissolve 34·5 grms. of Seignette salt and 10 grms. of NaHO in water, making this solution also up to 500 c.c. when cool. Measure off exactly 50 c.c. of each, cover the mixture with the layer of oil, and add the sugar solution at 80° to 85°.

As was revealed by Soxhlet's researches, the reducing power of sugars depends, not only on the concentration of the alkaline copper solution, but also on the strength of the sugar solution, and the same is observable in the case of the present reagent.

100 c.c. of the weaker solution (= $\frac{1}{10}$ normal Fehling) required for its reduction 0·044 grm. of glycose in 0·5 per cent solution. The same quantity of the double strength solution took 0·0806 grm. of glycose (in 0·5 per cent solution) to produce decolourisation. Stronger solutions of glycose exert a more powerful reducing action, and *vice versa*. For instance, 100 c.c. of ammonio-cupric solution are reduced by 0·0801 grm. of 1 per cent glycose, while 0·0821 grm. is necessary in the case of a 0·1 per cent solution.

In order to make this process available for analytical work, tables had to be calculated showing the amount of sugar, in various degrees of dilution, required for the reduction of 100 c.c. of the reagent solution, regard being chiefly had to the behaviour of glycose, invert sugar, invert in presence of saccharose, milk sugar, and maltose.

A.—*Glycose.*

A pure preparation, repeatedly re-crystallised from methyl alcohol, was taken, and the determinations made with solutions from 1 per cent down to 0·1 per cent strength. The amount of glycose required for the reduction increases fairly regularly with the degree of dilution.

The following table shows the amounts in c.c. and m.grms. of glycose of various degrees of concentration required for the reduction of 100 c.c. of ammonio-cupric solution, and will give a regular curve, provided the highest degrees of concentration are excluded. The figures will be found suitable for use in analysis, omitting the second place of decimals, as the accuracy of the method does not extend so far.

TABLE I.

100 *c.c. of Ammonio-cupric Solution are Reduced by a Solution of Glycose.*

Percentage strength of glycose solution.	C.c. of glycose required.	= M.grms. of glycose.
1·0	8·02	80·20
0·9	8·90	80·10
0·8	10·03	80·24
0·7	11·47	80·29
0·6	13·40	80·40
0·5	16·12	80·60
0·4	20·20	80·80
0·3	27·05	81·15
0·2	40·80	81·60
0·1	82·10	82·10

B.—*Invert Sugar.*

This sugar was prepared, according to Soxhlet's method, from saccharose purified by re-crystallisation from alcohol, 9·5 grms. being dissolved in 500 c.c., and, after addition of 200 c.c. of decinormal hydrochloric acid, inverted for thirty minutes on the water-bath, and finally made up to 1000 c.c. when cooled.

This, diluted to the same degree as the glycose solution, displayed, on testing, a reducing effect having a ratio of 94·9 : 100 as compared with the latter, their behaviour being similar.

TABLE II.

100 *c.c. of Ammonio-cupric Solution are Reduced by Invert Sugar Solution.*

Percentage strength of invert solution.	C.c. of invert sugar consumed	= M.grms. of invert sugar.
1·0	8·40	84·00
0·9	9·37	84·33
0·8	10·55	84·40
0·7	12·07	84·49
0·6	14·12	84·72
0·5	17·03	85·15
0·4	21·33	85·32
0·3	28·63	85·89
0·2	43·25	86·50
0·1	87·03	87·03

C.—*Invert Sugar in presence of Saccharose.*

In order to test the influence of saccharose on the reagent solution three series of experiments were made with 0·2, 0·5, and 0·8 per cent solutions of invert, containing varying amounts of saccharose, from 1 to 30 grms. per 100 c.c. The results showed the reducing power of saccharose to be extremely weak, 1 grm. of saccharose only producing the same effect as 0·0023 grm. of invert.

Application of the Test.

One preliminary experiment and two exact determinations are necessary, proceeding as follows:—

Measure into a dry beaker 50 c.c. of the ammonio-cupric solution from a burette, to which add from a pipette 50 c.c. of the alkaline Seignette solution, so that all the copper is washed off the sides of the glass, and immediately cover the liquid with a layer of pure paraffin oil about 0·5 c.m. deep. Heat the liquid carefully over wire gauze up to 80°—measured by the thermometer serving as a stirring-rod—and run in down the side of the vessel the sugar solution out of a Geissler burette tapped in front, so that the burette itself may stand on one side and be shielded from the heat of the flame by a sheet of asbestos. The sugar is added by c.c., the mixture being carefully stirred between whiles, and the temperature should be between 80° and 85°. Arrived at the point when the addition of 1 c.c. decolourises the liquid, the second experiment is proceeded with. This consists in an exact repetition of the first, except that the sugar is run in at once, and that 1 c.c. less of sugar is taken, so that the liquid remains blue. Now push the beaker away from the point of the burette and wash down the sugar on the side of the glass with 10 drops of water from a pipette. Then bring the temperature up to 85° again in two minutes, and continue adding the sugar by $\frac{1}{10}$ths of a c.c., with gentle stirring, until the colour disappears. As, notwithstanding the oil layer, the liquid gradually oxidises, the whole reaction, from the first addition of the sugar until complete decolourisation, should be carried out in five minutes.

The third test is a check repetition of the second.

The author cites typical analyses showing the concordant results obtained by his method.

Appointment.—Mr. Leo Taylor, F.I.C., F.C.S., has been appointed Public Analyst for Hackney, in succession to the late Dr. Tripe.

VARIATION IN THE AMOUNT OF FREE AND ALBUMENOID AMMONIA IN WATERS, ON KEEPING.

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

(Continued from p. 226).

Table IV.

Five Bottles each, Urine and Horse Pond Waters.

Temp. °F. Morn.	Ev.	Nos.	Date.	Horse Pond. Free NH_3.	Horse Pond. Alb. NH_3.	Urine and Distilled Water. Free NH_3.	Urine and Distilled Water. Alb. NH_3.
70	72	1	Nov. 3	0·35	0·08	0·09	0·012
74	76	2	„ 7	0·20	0·08	0·18	0·12
74	76	3	„ 11	0·05	0·08	0·18	0·12
74	76	4	„ 13	0·05	0·08	0·19	0·11
75	75	5	„ 14	0·03	0·07	0·21	0·12

In all cases where mixtures gave such large amounts of ammonia as to be unworkable they were, at the time of mixing, diluted with the requisite quantity of distilled water to bring the ammonia down to working limits.

The second of the above series (urine and distilled water) did not contain enough bottles; the amount of free ammonia increased from 0·09 to 0·21 in 11 days; if the experiment had been carried on for a longer time a larger amount might have been set free.

Table V.

Five Bottles each, Urine and Horse Pond Water.

Temp. °F. Morn.	Ev.	Nos.	Date.	Horse Pond and Garden Tank. Free NH_3.	Horse Pond and Garden Tank. Alb. NH_3.	Urine and Distilled Water. Free NH_3.	Urine and Distilled Water. Alb. NH_3.
76	76	1	Nov. 16	0·60	0·18	0·56	0·56
72	75	2	„ 21	0·01	0·13	1·20	0·39
74	76	3	„ 22	0·01	0·13	1·28	0·35
72	72	4	„ 24	0·01	0·11	2·56	0·29
66	69	5	„ 27	0·01	0·11	1·60	0·32

Note.—Rain on Nov. 11th.

In the second series containing urine the gradual increase and then decrease of free ammonia is very marked, the decrease of albumenoid ammonia going on very regularly.

Table VI.

Twelve Bottles Garden Tank Water and Urine.

Temp. °F. Morn.	Even.	Nos.	Date.	Free NH_3.	Alb. NH_3.
72	72	1	Nov. 24	0·27	0·27
66	69	2	„ 27	0·32	0·18
66	68	3	„ 29	0·20	0·18
67	68	4	„ 30	0·20	0·18
68	68	5	Dec. 1	0·16	0·15
66	71	6	„ 4	0·28	0·36
73	73	7	„ 6	0·36	0·40
76	77	8	„ 7	0·24	0·27
77	78	9	„ 8	0·17	0·15
73·5	75	10	„ 11	0·16	0·14
77	76	11	„ 12	0·14	0·13
71·5	72	12	„ 13	0·13	0·10

Note.—No rain from Nov. 11th.

If only the last two bottles of the above had been examined the impression conveyed would have been very different to that from the earlier and intermediate ones. Hence a very seriously contaminated water (were the ammonia tests solely relied upon) might, if kept for a few weeks, be passed as a fair or even good water.

(To be continued).

ON DEXTROSEBENZHYDRAZIDE.

By HEINRICH WOLFF.

Some time ago Herzfield and the author, and subsequently the author alone, had reported on the combination of dextrose and amidoguanidine, and in the meantime the author has obtained the compounds of amidoguanidine with galactose and lactose, on which I shall in future report in full. Although these compounds crystallise beautifully they are very soluble in water, and hence not suitable for separating the aldoses from other sugars. Now amidoguanidine may be regarded also as hydrazine, in which an atom of hydrogen of the diamide is replaced by the guanidine complex, that is, as guanidine hydrazine. It seemed therefore probable that also the hydrazides in which a hydrogen atom of the hydrazine is substituted by an acid residue should react with the aldoses, especially as phenylhydrazine also reacts.

The first compound of this kind, arabinosenitrobenzhydrazide, was obtained by Redenhausen at the instigation of Herzfeld, whilst the writer obtained dextrosebenzenesulphonhydrazide and dextrosebenzhydrazide.

Benzhydrazide was first produced by G. Struve, a pnpil of Curtius.

The reaction between the aldoses and the acidylhydrazides ensues according to the following equation:—

$$R:C:O.NH.NH_2+O:C.H.R. = $$
$$= R.C.O.N.H.N:C.H.R + H_2O.$$

The production is effected as follows:—The finely-powdered aldose and the hydrazide, the latter in slight excess, are introduced into an Erlenmeyer flask, covered with alcohol at 96 per cent, and heated five or six hours in the reflux refrigerator. If sufficient alcohol has been taken the whole dissolves, but if the alcohol is insufficient the compound formed is re-precipitated, and the liquid begins to bump. We then evaporate nearly to dryness on the water-bath, when the whole congeals to a paste of fine needles, which subsequently becomes solid. If the reaction has not been completed on boiling, it is hereby brought to an end, and it is allowed to cool, when the substance separates out in fine needles, which are filtered off and are re-crystallised from alcohol.

Dextrosebenzenesulphonhydrazide.—This compound is formed according to the equation—

$$C_6H_5SO_2NH.NH_2+C_6H_{12}O_6=$$
$$=C_6H_5SO_2NH.N:C_6H_{12}O_5+H_2O.$$

It is prepared in the manner indicated. Its composition is $C_{12}H_{18}N_2O_7S$. It separates from alcohol in white needles, which melt at 154° to 155°, with a brown colour and decomposition. In cold water it is rather sparingly soluble, and can be re-crystallised from water in the form of small rhombic crystals, which form crusts; but the temperature must not exceed 70°; as soon as bubbles of gas rise out of the liquid, decomposition sets in. The substance is lævo-rotatory, moderately soluble in hot alcohol, sparingly in cold alcohol, insoluble in ether.

Dextrosebenzhydrazide is formed from dextrose and benzhydrazide, according to the equation—

$$C_7H_8N_2O+C_6H_{12}O_6=C_{13}H_{18}N_2O_6+H_2O.$$

Its composition is $C_{13}H_{18}N_2O_6$. Crystallises from alcohol in white needles, which melt with decomposition at 171° to 172°, turning brown. Its conditions of solubility are almost the same as those of the benzenesulphonehydrazide compound, and it is also lævo-rotatory.

Scission of Dextrosebenzhydrazide.—If this compound is boiled in water it is split up smoothly into dextrose and benzhydrazide, as mentioned by Radenhausen. If benzaldehyd is added, drop by drop, insoluble benzalbenzhydrazide is at once precipitated. It is convenient to proceed as follows:—Dextrosebenzhydrazide is dissolved in hot water in an Erlenmeyer flask, the calculated quantity of benzaldehyd is added, and the whole is boiled for

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* Read before the Australasian Association for the Advancement of Science, Brisbane, January, 1895.

about five minutes with constant agitation. It is then allowed to cool, the benzalbenzhydrazide is sucked off, and the filtrate is again boiled with the addition of a little benzaldehyd to ascertain if the reaction is complete. The filtrate is evaporated to dryness, taken up with a little cold water in order to remove traces of benzalbenzhydrazide, evaporated again, taken up with alcohol, and precipitated with ether to remove benzaldehyd and benzoic acid, repeating the operation if necessary. The dextrose is then quite pure.

The cause of the scission may be most readily seen in dextrosebenzenesulphonhydrazide. If, namely, benzenesulphonhydrazide alone is heated in water, the following reaction occurs:—

$$2C_6H_5SO_2NH.NH_2 = C_6H_5.SO_2.N.H.NH.SO_2.C_6H_5 + \\ + N_2.H_4.$$

A single ebullition is sufficient to produce this result. Hence if dextrosebenzenesulphonhydrazine is evaporated down with water, the following reaction takes place:—

$$2C_6H_{12}O_5.N.NH.SO_2C_6H_5 + 2H_2O = \\ = 2C_6H_{12}O_6 + 2N : H_2.NH.SO_2C_6H_5.$$

The latter, as above stated, forms at once dibenzenesulphonhydrazide (with a violent escape of gas), and behaves with the sugar like a strong acid.

As the benzhydrazide passes into dibenzhydrazide only at a high temperature, we may perhaps assume that the tendency to this change is the primary cause of the scission.—*Berichte*, xxviii., No. 2, p. 160.

THE DETECTION OF BLOOD-SPOTS, ESPECIALLY IN PRESENCE OF RUST.

By Herren MECKE and WIMMER.

The authors recommend the observation of the absorption spectrum of oxyhæmoglobine in the following manner:—

Some particles of a spot occurring on iron are placed on a port-object, touched with a small drop of water, and heated for a short time to about 30°, replacing the water as it evaporated. If the spot was old and dried up in a thin layer, the chief part of the colouring-matter of the blood is oxidised to methæmoglobine. In order to reconvert it into oxyhæmoglobine they add to the solution on the port-object a trace of a solution of tartaric acid, ferrous sulphate, and excess of ammonia, by means of a glass rod drawn out to a fine point. Along with the drop they lay on the port-object a horse-hair, and over all a covering glass. By cautiously raising the superimposed corner the drop of liquid is moved to the middle of the covering-glass, under which a second horse-hair is pushed. The drop now forms a minute column between the port-object and the covering-glass, the depth of which needs to be merely 1 m.m. in order to obtain an observation of the absorption-spectrum. In this manner we may operate with 0·5 cubic millimetre, or only 0·0005 grm. of liquid. If no micro-spectrum apparatus is available, the edges of the covering-glass are fixed to the port-object with melted wax or paraffin, the eye-piece and the illuminating arrangement are removed, and the microscope is placed in a horizontal position. The spectroscope is set in front of the microscope in such a manner that the tube of the latter lies in a straight line with the slit-tube of the former, the object is illuminated in a suitable manner, and the absorption-spectrum is examined.

If the stains are dried upon cloth it is digested in water, the liquid is evaporated down to a small volume, and a trace of ammonium sulphide is added, which effects the transformation of methæmoglobine more speedily. This reagent is not applicable in presence of rust, in consequence of the formation of iron sulphide.

Less sharp spectra are obtained after drying up the solution of blood upon some fibres of linen or white silk, laid close together and moistened with glycerin containing ammonium sulphide, covered with a covering-glass, and then examined with the micro-spectroscope.

The reduction-liquids must in all cases be added cautiously, to prevent the formation of hæmoglobine, the absorption-band of which is not so distinct as the absorption-bands of oxyhæmoglobine.

If suspicious spots are found on articles of iron, solution in hydrochloric acid often gives a clue to their nature. If a few particles of the substance in question are heated on the port-object with hydrochloric acid, the solution contains flocks if blood is present.

The guaiacum test for blood has been recently recommended by Schär. He pronounces a spectroscopic examination, and the production of crystals of hæmin, the most certain methods, and indispensable in the conduct of forensic investigations, but the guaiacum test is still valuable.

It has been urged as an objection that nitrous acid and other oxidising agents turn the tincture of guaiacum blue; but these substances react *without* an addition of oil of turpentine, and are thus sufficiently distinguished from blood. The latter (and also hæmatine) transfer oxygen from ozonised blood to guaiacum resin, thus rendering its constituent guaiaconic acid blue. This property (of acting as a transferrer of ozone) is shared by blood after it has been heated to about 100°; it is therefore not dependent on any ferment present in blood.

For the detection of small quantities of blood Schär mixes the aqueous liquid in question with tincture of guaiacum, and filters. This tincture consists of 1 grm. of the resin in 100 c.c. of absolute alcohol. There remains on the filter finely-divided resin along with constituents of blood, if blood was present. The filter is then shaken up in Hänefeld's mixture (consisting of oil of turpentine, alcohol, and chloroform, 200 parts of each; glacial acetic acid and water, 2 parts of each). The presence of blood is shown by a blue colour. A negative result of this test proves the *absence* of blood, but a positive result is no certain demonstration of its presence. —*Zeitschrift fur Analyt. Chem.*, and *Pharm. Zeit.*

THE USE OF SODIUM PEROXIDE IN ANALYSIS.

By Herren HEMPEL, SPULLER, KALMAN, and POLECK.

This reagent, exceedingly rich in oxygen, is more suitable than any other substance for oxidations at a red-heat.

If we mix chromiferous or manganiferous substances with about twice their weight of the peroxide, and heat on sheet-silver or platinum, the mixture becomes almost immediately deep yellow or green. Tungsten mineral, if mixed with 4 parts of the peroxide, gives in a few minutes a melt from which sodium tungstate can be easily extracted on treatment with water.

Titaniferous iron ore can be opened up in a very short time by mixture with 4 parts of sodium peroxide, and fusion in a silver crucible. The melt is extracted with hot water; the precipitate, containing ferric oxide and the titanic acid, is placed without washing in a platinum crucible along with concentrated sulphuric acid, which is evaporated down to a slight residue. Hence we obtain all the titanic acid in solution if the liquid, when quite cold, is poured into a large quantity of cold water. If the solution is not perfectly clear it is filtered, and then the titanic acid is separated as usual by prolonged ebullition, with the introduction of sulphurous acid.

Sulphur compounds are oxidised with explosive violence. For determining sulphur Hempel uses, to 1 part of the substance in question, 2 parts soda and 4 parts of peroxide, and melts the mixture in a silver crucible. The chief part of the melt is conveniently poured into a capsule of silver, nickel, or platinum, standing in cold water. It is filtered, acidified with hydrochloric acid, and precipitated with barium chloride.

For the complete analysis of blende and galena it is also recommended to open up with sodium peroxide, since the iron is at once separated as oxide, whilst lead and zinc pass into the alkaline liquid.

J. Spuller and S. Kalman have also made experiments which lead to analytical methods. They have successfully oxidised with sodium peroxide ferrochrome, chrome-steels, chrome-iron ore, and sulphur ores.

The experiments of Poleck are also interesting. Whilst a great number of organic liquids—glacial acetic acid, benzaldehyd, ether, &c. — are at once ignited, ethylic alcohol behaves quite differently; substances dissolved in alcohol can be easily oxidised by sodium peroxide. Iodine was oxidised to periodic acid, lead to sodium orthoplumbate. On the other hand, salts of silver and mercury, as also potassium permanganate, were reduced. —*Zeit. fur Anorg. Chemie* and *Chemiker Zeitung.*

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Anniversary Meeting, April 25th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. Francis H. Carr, A. T. Cocking, Alexander Hogg, and Frank Newbolt were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Edgar S. Barralet, 61, Thistlethwaite Road, Clapton, N.E.; Gustav Theodore Bruckmann, B.Sc., 192, 18th Street, Brooklyn, N.Y.; Walter W. Cheadle, B.A., 19, Portman Street, W.; Sydney Fawns, 16, Onslow Gardens, S.W.; Alexander F. Fuerst, Ph.D., 30, Belsize Road, N.W.; William Goddard, 11, Granville Road, Middlesbrough; Patrick Hope Grant, 57, S. Guildry Street, Elgin, N.B.; William Abraham Greaves, B.Sc., Bankside, Golden Valley, Alfreton; Charles Butterworth Newton, Gasworks Rotherham; Frank L. Slocum, Pittsburgh, Pa.; Alfred Stanfield, B.Sc., 21, Markham Square, S.W.; William Thomas Thomson, Austin Villas, Station Road, Waltham Cross; Arthur Thornton, M.A., 67, St. Mary's Terrace, Manningham; William Arthur Whiston, Collegiate School, Llandudno; John Wilson, B.Sc., 11, Cupar Road, Battersea, S.W.

Of the following papers those marked * were read:—

*45. "*Action of Nitrosyl Chloride on Amides.*" By WILLIAM A. TILDEN, F.R.S., and M. O. FORSTER, Ph.D.

The authors find that the interaction of nitrosyl chloride and amides generally results in the exchange of the amidogen group, NH_2, for an atom of chlorine; but as a molecule of water is formed simultaneously, the chloride produced is converted into the corresponding acid more or less completely according to the conditions of the experiment. Acetamide, benzamide, malonamide, oxamic acid, urea, and urethane behave in this way.

Glycocine and asparagine, as examples of amido-compounds, give the corresponding chloro-acid.

Oxamide is entirely unaffected by nitrosyl chloride at any temperature up to 100°. Oxanilide, hippuric acid, succinimide, and phthalimide are also unattacked.

Since glycocine and asparagine (or aspartic acid) exchange NH_2 for Cl like the amides, the authors regard this as confirming the formulæ by which these substances are represented as amido-derivatives of acetic and succinic acids respectively. They consider the closed chain formulæ, lately revived by Sakurai, to be inadmissible.

*46. "*Action of Nitrosyl Chloride on Asparagine and Aspartic Acid; Formation of Lævorotatory Chlorosuccinic Acid.*" By WILLIAM A. TILDEN, F.R.S., and B. M. C. MARSHALL.

The authors have studied the products of the action of nitrosyl chloride on asparagine dissolved in hydrochloric acid, and more especially the resultant chlorosuccinic acid. This substance crystallises in short lustrous prisms, it melts at about 174° with decomposition, and is lævorotatory, $[\alpha]_D = -19{\cdot}67^\circ$, at the temperature of the air. The silver and copper salts may be obtained as precipitates nearly insoluble in water. The acid agrees closely in melting-point with the dextrorotatory chlorosuccinic acid obtained from malic acid by Walden, and the values for the specific rotatory power of the two compounds are nearly the same. Walden's acid showed a specific rotatory power of 20·6° to 20·8°. The lower value for the lævorotatory acid is probably due to its partial dissociation into hydrogen chloride and fumaric acid when dissolved in water.

*47. "*A Property of the Non-luminous Atmospheric Coal-gas Flame.*" By LEWIS T. WRIGHT.

The author points out that the separation of the atmospheric gas flame (Bunsen flame) into two distinct parts described by Teclu (*J. Pr. Chem.*, xliv., 246) and Smithells and Ingle (*Trans.*, lxi., 204), was discussed by himself in June, 1887, in a paper "On the Induction of the Explosive Wave and an Altered Gaseous Condition in an Explosive Gaseous Mixture by a Vibratory Movement," an abstract of which was published in *Roy. Soc. Proc.*, xlii.

The experiments described in that paper were made with a mixture of coal-gas and air in combustion tubing of ¾ in. diameter.

The analytical results of that enquiry confirm those obtained by Smithells and Ingle, and bring out a characteristic of the inner flame. It is able to maintain a stationary position in the glass tube against various velocities of egress of the gaseous mixture. The distribution of the oxygen amongst the three principal products of combustion, viz., carbon monoxide, carbon dioxide, and water, differs, however, with the velocity of the gaseous current in the tube. The carbon dioxide increases, and the carbon monoxide decreases with increased velocity of the gaseous current.

*48. "*Diortho-substituted Benzoic Acids. I. Substituted Benzoyl Chlorides.*" By J. J. SUDBOROUGH, Ph.D.

In this paper, the author, after referring to the work of V. Meyer and Sudborough on the esterification of aromatic acids—in which it is shown that diortho-substituted benzoic acids as a rule yield no esters, when their alcoholic solutions are saturated with dry hydrogen chloride—describes the preparation and properties of the following substituted benzoyl chlorides. *o*-, *m*-, and *p*-Brombenzoyl chloride; 2·4, 3·5, and 2·6 dibrombenzoyl chloride; 3·4·5 and 2·4·6-tribrombenzoyl chloride; 2·3·4·6-tetrabrombenzoyl chloride; 2·6-dinitrobenzoyl chloride; 2·4·6-trinitrobenzoyl chloride; together with the acid amides and esters obtained from them.

In each case, experiments were made by boiling 0·5 grm. of the acid chloride with 20 c.c. of an 8 per cent solution of pure sodium hydrate. These experiments have shown—

1. That the acid chlorides which do not contain bromine atoms in the ortho-positions are readily decomposed, in most cases, before the solution begins to boil, in the others within ten seconds of boiling.

2. That those acid chlorides which are substituted by one bromine atom in an ortho-position are somewhat more stable, and are only completely decomposed after boiling for two to three minutes with the alkaline solution.

3. That acid chlorides with bromine atoms in the two ortho-positions are extremely stable.

Thus, while the 2·6-dibrombenzoyl chloride is entirely decomposed after boiling for thirty-five minutes with the alkaline solution, only 28—30 per cent of the 2·4·6-tribrom chloride is decomposed after boiling for one hour. and of the tetrabrom chloride from 6 to 8 per cent is decomposed after boiling for the same length of time with the caustic soda solution.

The decomposition of the di- and tri-nitrobenzoyl chlorides could not be quantitatively followed, as other reactions occur at the same time, and a deep red solution is formed in both cases.

The author intends investigating the corresponding methyl- and chlorbenzoyl chlorides in order to see whether the same rules hold for these as for the bromderivatives.

*49. "*Diortho-substituted Benzoic Acids. II. Hydrolysis of Aromatic Nitriles and Acid Amides.*" By J. J. Sudborough, Ph.D.

For the preparation of large quantities of substituted benzoic acids from the corresponding nitriles, the author recommends a modified form of the method suggested by Bouveault (*Bull. Soc. Chim.*, [3], 9, 368). Whereas Bouveault states that the method is only applicable to those nitriles which are converted into the acid amides by heating with 90 per cent sulphuric acid for several hours on the water-bath; the author of this paper shows that the method can be used for other nitriles, provided the sulphuric acid mixture is heated on the sand-bath to 120—130° for an hour or so. The acid amides thus obtained are converted into the corresponding acids by means of sodium nitrite according to Bouveault's method. The yields are extremely good and it would seem that the method is of very general application. The following acids have been obtained by the method:—

p-Brombenzoic acid, 2·4, and 2·6-dibrombenzoic acid, 2·4·6-trichlorbenzoic acid.

The 2·6-dibrombenzoic acid is readily soluble in water and separates out on standing in the form of long needles or short prisms of m. p. 146·5°.

The 2·4, and 2·6-dibrombenzamides, which were obtained as intermediate products in the preparation of the corresponding acids, differ most remarkably in their properties. Thus, whilst the 2·4-compound is completely converted into the correspending acid by heating to 170—180° in a sealed tube with 80 per cent sulphuric acid, the 2·6-amide under the same conditions is entirely unacted upon.

This behaviour of the two amides is quite analogous to that of the corresponding acid chlorides towards alkalis (see preceding abstract). A study of the work of Claus and his pupils (*J. Pr. Chem.*, [2], xxxvii., 197; *Annalen*, cclxv., cclxvi., cclxix., cclxxiv.) on the hydrolysis of various substituted aromatic nitriles, shows that the diortho-substituted benzamides are, as a rule, remarkably stable towards hydrolysing agents. Thus, while substituted benzonitriles are converted into the corresponding acids by boiling for some time with fairly concentrated sulphuric acid, those nitriles which are substituted in the two ortho-positions yield the acid amides and not the acids under the same treatment. An important exception to this rule appears to be the 2·6-dichlorbenzamide, as Claus and Weil state that the 2·6-dichlorbenzonitrile is directly converted into the acid when heated with sulphuric acid in sealed tubes at 150°. This appears remarkable when compared with the behaviour of the corresponding brom-compounds, and the author hopes to investigate the hydrolysis of various substituted benzamides.

*50. "*Note on the Action of Sodium Ethylate on Deoxybenzoïn.*" By J. J. Sudborough, Ph.D.

In attempting to prepare substitution-derivatives of deoxybenzoïn, $C_6H_5 \cdot CO \cdot CH_2 \cdot C_6H_5$, by heating together deoxybenzoïn, sodium ethylate, and various halogen compounds in sealed tubes at 150—160°, the author always observed the production of a considerable quantity of stilbene (diphenylethylene). Experiments have shown that this is produced by the action of sodium ethylate on deoxybenzoïn at 160°, and that a substance which is very soluble in alcohol, and has a much lower m.p., is formed at the same time. On analysis this latter compound proved to be hydroxydibenzyl, $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot C_6H_5$. It is evidently produced from the deoxybenzoïn by the reducing action of the sodium ethylate. This compound, when heated, loses water, and is converted into stilbene. The hydroxydibenzyl, when re-crystallised from hot ligroin (b.p. 40—50°), forms long, silky needles which melt at 63°.

When deoxybenzoïn is heated with sodium methylate no trace of stilbene is formed. This is interesting when compared with the results obtained by Lobry de Bruyn on the action of sodium ethylate and methylate on various aromatic nitro-compounds.

De Bruyn shows that whilst the methylate acts as a substituting agent, replacing a nitro- by a methoxy-group, the ethylate at the same time acts as a reducing agent, producing more or less of the corresponding azo-compounds.

51. "*A Constituent of Persian Berries.*" By A. G. Perkin and J. Geldard.

Persian berries, as is well known, contain a glucoside xanthorhamnin (α-rhamnegin) decomposable by acids into isodulate and a colouring-matter rhamnetin. With hydriodic acid rhamnetin yields methyl iodide and quercetin, the colouring-matter of quercitron bark (Herzig, *Monatsch.*, ix., 548—561). It is consequently a quercetin monomethylether, $C_{16}H_{12}O_7$. According to earlier workers there is also present a second glucoside which gives a colouring-matter more soluble in alcohol than rhamnetin, and therefore called β-rhamnetin. Herzig (*Monatsch.*, x., 561—567), when studying this subject, isolated from the berries a glucoside which he regarded as a loose double compound of xanthorhamnin and a glucoside of quercetin (quercitrin ?), for by decomposition it gave a mixture of rhamnetin and quercetin. Hence β-rhamnetin appeared to be quercetin.

In this paper it is shown that Persian berries contain a third substance readily isolated from the mixed colouring-matters by extraction with toluene. It forms long yellow needles somewhat resembling anthraquinone, melting at 214—215° (quercetin and rhamnetin both melt above 280°), has the formula $C_{17}H_{14}O_7$, and crystallises from acetic acid with 2 mols. of acetic acid of crystallisation. The triacetyl compound $C_{17}H_{11}O_7(C_2H_3O)_3$, colourless needles, melts at 154—155°; the tribenzoyl compound $C_{17}H_{11}O_7(C_7H_5O)_3$, colourless needles, melts at 204—205°; and the dibromo-compound $C_{17}H_{12}O_7Br_2$, yellow needles, decomposes at 250° before melting. By the action of hydriodic acid it yields quercetin and 2 mols. of methyl iodide, and is therefore a *quercetin dimethyl ether*. Rhamnazin, as we have called this substance, is nearly devoid of dyeing properties. Quercetin being a colouring-matter, contains at least two hydroxyls in the ortho position to one another, and in rhamnazin therefore one or two of these hydroxyls must be replaced by a methoxy group, causing this loss of colouring power.

It is known that an aqueous extract of Persian berries ferments at 30—40°, depositing a yellow powder, the supernatant liquid being of an orange-brown colour. This powder is here shown to be a mixture of rhamnetin and rhamnazin with but a trace of quercetin. The supernatant liquid when boiled with acids gives a considerable quantity of quercetin only. It appears therefore that the ferment contained in the berries (Ward and Dunlop, *Annals of Botany*, 1889), while readily decomposing xanthorhamnin and the glucoside of rhamnazin at this temperature, exerts but little influence upon the glucoside of quercetin also present.

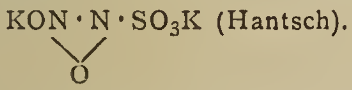
The colouring-matters of Persian berries are rhamnazin quercetin dimethyl ether), rhamnetin (quercetin mono-(methyl ether), and quercetin, $C_{15}H_{10}O_7$, itself.

52. "*Potassium Nitrososulphate.*" By E. Divers, F.R.S., and T. Haga.

According to Raschig, there are two salts of the composition of Pelouze's potassium nitro(so)sulphate, prepared almost in the same way from nitric oxide and potassium sulphite. Hantzsch has recently (*Ber.*, xxvii., 3264) investigated this matter in connection with his studies of the stereoisomerism of nitrogen compounds, and finds that he cannot get the salt like Pelouze's salt, which Raschig got, but only one which is identical with Raschig's other, or second, salt. There are therefore, it would seem, two isomeric salts, one being Pelouze's salt and the other Hantzsch's. Raschig alone got both these salts.

The authors are convinced that no isomer of Pelouze's salt has been shown to exist. In the first place, Raschig and Hantzsch have confounded the former's first salt with Pelouze's, through supposing that the latter salt is precipitable by dilute solutions of barium salts. In the second place, this first salt prepared by Raschig appears, from his description, to have been so particularly like another obscurely known salt obtained by him, and called "basic potassium dihydroxylaminesulphonate," as to be at present almost indistinguishable from it (as described), whether in composition, in chemical properties, or even in preparation, if only, as might have happened, some nitric peroxide or air got into the sulphite solution along with the nitric oxide. In the third place, a re-examination of Pelouze's salt, in the light of Hantzsch's observations, shows that no sufficient grounds exist for asserting the non-identity of Hantzsch's salt, or the second salt of Raschig's, with Pelouze's salt.

The authors point out that nitrososulphates do not show such near analogy to isonitramines as Traube believes them to do, and regard them as displaying the constitution of a sulphate, $KON_2{\cdot}O{\cdot}SO_3K$, rather than that of a sulphonate,—



$$\underbrace{KON\cdot N}_{O}\cdot SO_3K \text{ (Hantsch).}$$

Potassium nitrososulphate behaves like a sulphonate in giving a barium-potassium salt (and so also does potassium ethyl sulphate, though a true sulphate), but it also gives barium sulphate instantaneously when acidified, and no sulphonate does that.

53. "*The Milk of the Gamoose.*" (Second notice). By H. Droop Richmond.

In a previous paper (*Trans.* lvii., 758) the author described a sugar existing in the milk of the gamoose, differing in its properties from milk sugar. He now finds that this sugar is not always present in the milk of these animals, and describes experiments showing the difference between milk examined in January, 1890, and August, 1891.

PHYSICAL SOCIETY.

Ordinary Meeting, May 10th, 1895.

Captain W. de W. Abney, President, in the Chair.

Mr. Herroun read a paper "*On the Iodine Voltameter.*"

After referring to the usual methods of determining the value of the small currents used in calibrating galvanometers and other apparatus for measuring small currents, and discussing the errors to which they are subject, the author gave his reasons for selecting iodine. He did this since, with the exception of mercury in the mercurous state, iodine has the largest electro-chemical equivalent, and, in addition, by titration with sodium thiosulphate, it is possible to determine the quantity of iodine liberated with a greater accuracy than can be obtained by weighing a deposit of copper or silver with the balance. The solution employed in the voltameter contains 10 to 15 per cent of zinc iodide. If care is taken to leave a small piece of metallic zinc in this solution, no free iodine is liberated on keeping, unless the solution is exposed to a strong light for some time. The anode consists of a plate of platinum at the bottom of a tall and fairly narrow beaker. The wire leading the current to the anode is encased in a glass tube, so that the iodine is only liberated at the bottom of the beaker, where, on account of its great density, it tends to collect. The kathode consists of an amalgamated zinc rod, which, to prevent loose particles of zinc falling down into the iodine, is surrounded by a piece of filter-paper or vegetable parchment. In an electrolysis lasting for as long as two hours none of the iodine is found to diffuse up to the part of the solution near the zinc kathode. Where, on account of the extreme feebleness of the currents employed, it is necessary to allow the electrolysis to continue for longer than two hours, a U-tube is used with two small plugs of asbestos at the bend, the anode being in one limb and the kathode in the other. With this form of voltameter, even after the current has flowed for several days, no signs of iodine have been found in the limb containing the kathode. On account of the production of electric convection currents, the iodine voltameter does not seem to be quite so suitable for the accurate measurement of strong currents.

After the current is stopped the zinc electrode is immediately removed, the solution stirred, and the amount of iodine liberated determined by titration with sodium thiosulphate. The author finds that a convenient strength of the thiosulphate solution is one in which 1 c.c. corresponds to the amount of iodine liberated by 5 coulombs of electricity. This solution contains 12·8375 grms. of pure crystallised sodium thiosulphate per litre. It is possible to perform the titration to within 0·1 c.c., which corresponds to 0·5 coulomb, or if the electrolysis lasted one hour to $\frac{1}{7200}$ ampère. In a comparison made with a silver voltameter, the current as deduced from the silver was 0·0264 ampère, and that deduced from the iodine 0·0266. The author considers that part of the difference may be due to the effect of oxygen dissolved in the silver nitrate.

Prof. Carey Foster considered this process for measuring currents a most valuable one. The idea of using a volumetric method for measuring currents was, to him, new. He did not, however, see the advantage of using a substance with a high electro-chemical equivalent if a volumetric method was employed to estimate the quantity of the substance liberated. It would be possible to use a chloride, though in this case the titration would probably be less accurate.

Prof. Silvanus Thompson said he thought the method would be very valuable, but he would like to know if any error was likely to arise if too great a current density was employed. The number the author had assumed for the atomic weight of silver (108) was only approximate; if the more accurate value 107·7 were used the agreement between the results obtained with the silver and iodine voltameters would be improved.

Mr. Trotter asked what was the largest current that could be accurately measured.

Mr. Enright said he had used porous diaphragms in iodine voltameters, and found that the iodine collected in the positive compartment, while the water was driven over into the negative compartment. With strong currents it was possible to get almost pure iodine left in the one compartment.

Mr. Watson thought that since the value for the electro-chemical equivalent of iodine used by the author was deduced from Rayleigh's value of the electro-chemical equivalent of silver, and that Rayleigh's experiments were performed in air, the difference obtained with the silver and iodine voltameters could hardly be due to the cause suggested.

Mr. Elder warned the members that volumetric measurements were not so accurate or easy as they seemed. He particularly mistrusted a solution of sodium thiosulphate, since he had found a solution of this substance to change even in twenty-four hours. The difficulty of accurately reading the burette might be overcome by weighing the burette and its contents before and after the titration.

The author, in his reply, said that with the size of electrodes he used (about 9 sq. c.m. surface), 0·1 ampère was the maximum current it was safe to use. The only substance likely to be produced by too great a current density was periodate, which, since it was insoluble, would immediately be noticed. The influence of the dissolved oxygen was only appreciable with small currents where the electrolysis lasts some time; while in Rayleigh's experiments large currents were employed.

The Chairman, while returning thanks to the author for the paper, mentioned that in his experience he had found zinc salts to be very untrustworthy.

Mr. A. Sharp read a paper entitled "*A New Method in Harmonic Analysis.*"

The author in this paper applies the principle of the form of harmonic analyser for giving direct readings of the amplitude and epoch of the various constituent harmonic terms previously described by him, to the performance of harmonic analysis without the use of an instrument. The kinematic principle is as follows:—Let the curve to be analysed be drawn, with a scale of abscissæ such that the period is 2π. Let a wheel, w, roll on the paper and be connected with a tracing-point, P, in such a manner that as P moves uniformly in the x direction the axis of the wheel w turns uniformly counter clockwise in a horizontal plane, and the distance rolled through during any short interval is equal to the corresponding displacement in the tracer P in the y direction. The curve traced out by w the author calls the roller curve, and from the vector joining the initial and final points of this curve the amplitude and epoch can be determined. Suppose the periodic curve consists of a portion of the curve,

$$y = a_0 + a_1 x + a_2 x^2 + a_m x^m,$$

repeated over and over again; then if the tracer is taken round this periodic curve you get a rolled curve, which may be called the first rolled curve. If now the curve whose ordinates are—

$$\frac{d\,y}{d\,x}$$

is traced out, the roller curve obtained is the evolute of the first, and so on for—

$$\frac{d^2\,y}{d\,x^2}, \text{\&c.}$$

The author gives two worked examples, and compares the values of the coefficients obtained with those given by the harmonic analyser of the Guild's Central Technical College.

Prof. Henrici said he had not received the paper in time to thoroughly master it, but he thought that, at any rate for curves where no discontinuity occurred, the relation found by the author between the roller curves was always true, the last evolute being a point, and the one before that a circle. The interesting point was whether the method was capable of being used for practical purposes, for it occupied a place with respect to harmonic analysis similar to that occupied by Simpson's rule in planimetry.

Prof. Silvanus Thompson asked if the author had devised a form of mechanism capable of fulfilling the kinematical conditions given at the commencement of the paper.

The author, in his reply, said he had devised such a mechanism, and that it was described in his previous paper. In addition he had since invented a more practicable form, which he had patented.

The Chairman said the Society ought to congratulate itself on the large number of important papers dealing with harmonic analysis and planimetry that had lately been communicated.

NOTICES OF BOOKS.

Principles and Practice of Agricultural Analysis. A Manual for the Estimation of Soils, Fertilisers, and Agricultural Products. For the Use of Analysts, Teachers, and Students of Agricultural Chemisty. Vol. I.—Soils. By Harvey W. Wiley, Chemist to the U. S. Department of Agriculture. 8vo., pp. 607. Easton: Chemical Publishing Co. 1894.

In examining this elaborate work we may first give a glance at the author's nomenclature. He adopts a certain half-way reform in chemical terminology. Thus he deletes the final *e* in the names of the halogens and their compounds, as well as "oxid" and "sulphid." He writes "sulphur" with *f* instead of the traditional *ph*. But we may ask why, having gone so far, he does not take an additional step, which would not be in the least confusing to the reader? Why not, in the names of the halogens, simply eliminate the appendage "ine," and write fluor, chlor, brom, and iod? Why does he not cut off the needless "us" from phosphorus, and call this element simply *phosphor?* By so doing he would have given his support to a desirable improvement in the language of inorganic chemistry.

Turning from manner to matter, we must congratulate Mr. Wiley on the judicious thoroughness of his compilation. The volume before us, devoted to the consideration of soils, consists of eight parts, treating respectively of the origin of soils, of sampling for analysis, of the physical properties of soils, of mechanical—or, as it might perhaps be better called, physical—analysis, of the estimation of gases in soils, of the chemical analysis of soils, of the determination of nitrogen in its various states, and of the special examination of waters. Each of these parts concludes with a special bibliography. The remarks on the origin of soils suggest important questions connected with the genesis of organisms, but into these—as having no bearings on agricultural practice—the author does not enter. We may ask whether he does not go too far in regarding boron as a true plant-food, and whether he is not chargeable with a sin of omission in failing to condemn the use of boric acid as a food preservative? Manganese and copper have at last as good a claim to rank as plant-foods as has boron.

The importance of a microscopic examination of soils and rocks accompanying the chemical analysis is justly insisted on. The different agencies, vital and lifeless, which effect the disintegration and to some extent the decomposition of rocks, are discussed to some extent. The author holds that the power of ice in effecting "rock decay" has been somewhat over-rated, and that the entire absence of frost promotes the process. In discussing the evils of soils loaded with alkalies—one of the greatest enemies which the subtropical agriculturist has to encounter—he points out that irrigation without drainage intensifies the mischief. Peaty soils appear to bear in America the unpleasing name of "mucks."

The instructions for sampling soils are very useful. We have known analysts occur most unmerited blame for their reports on specimens unfairly taken.

In Part 3 we do not see it mentioned that the black colour of a soil may be due to sulphur compounds acting upon iron oxides.

The instructions for physical analysis are highly valuable, and bring into prominence not a few considerations which should not be neglected if analysts were allowed time to do justice to the specimens upon which they operate. Staining particles of silt for microscopical examination, as is done in case of bacteria, may often throw an instructive light upon the capabilities of a soil.

The 6th and 7th Parts, giving instructions for the chemical analysis of soils, and especially for the determination of their combined nitrogen, are very elaborate. Concerning manganese we find the admission that this element "exists in all plants, and its presence in small quantities seems necessary to vegetation." The method recommended for its determination is that of Leclerc. It is recognised that in some cases "the introduction of iron as a fertilising element may be useful."

Sodium chloride is—rightly according to our experience —regarded as injurious in the proportion of 1 lb. to 1000 lbs. of earth.

Concerning the supply of nitrogen to plants, the author does not recognise its absorption from the air without the co-operation of micro-organisms.

In Part 8, describing the analysis of agricultural waters, we find no mention of the method of Frankland. Its rival process is solely ascribed to Nessler. This chemist certainly discovered the reaction which here comes into play, but it is generally understood to have been rendered quantitative by Wanklyn, a fact never, we believe, denied in the long and bitter controversy on the merits of the two processes.

A few expressions to be encountered in this work will scarcely be understood on this side of the Atlantic. What, for instance, is a "truck farm"?

We hope that the second volume will prove equal in value to the one before us.

Organic Chemistry, Theoretical and Practical, adapted to the Requirements of the Science and Art Department, and of the London University. By Isaac Sydney Scarf, F.I.C., F.C.S., Professor of Chemistry and Experimental Physics in the City of London College, and a Science Master in the City of London School. With 36 Illustrations and 180 Experiments. Post 8vo. London and Glasgow: W. Collins, Sons, and Co., Limited.

It may perhaps be some faint consolation to the Chinese, amidst their reverses, to learn that the system of education which has helped so powerfully to keep them in a state of non-age, is still obstinately adhered to by a nation which proclaims itself the great incarnation of progress. No work ever published, in China or in Britain, could be more openly and avowedly examinational than the one before us. In its very title it is described as being "adapted to the Requirements of the Science and Art Departments, and of the London University." We must beg permission to express a conviction that the requirements of a Science and Art Department or of any true University should, on the contrary, be adapted to the state of Science!

In the Preface, brief as it is, we find further reference to the same subject. The book is said to be "written primarily for students preparing for the elementary examinations of the Science and Art Department." In the next sentence we are told that it contains "sufficient experimental matter to make it available as the laboratory companion of candidates for the Int. N.B. and final B.Sc. of the London University and other examinations." Lastly comes the further information that "certain portions of the work may be omitted by those who wish to qualify for a pass only in theoretical and practical organic chemistry." *Eheu!*

On the other hand, we are glad to perceive that the author is evidently not satisfied with the termination *ine* for the names of the alkaloids; at least he gives the form in *ia* as a synonym. We wish the example could be generally followed. The recent Inland Revenue ukase, by which methylated spirt is for most purposes spoiled by the addition of mineral naphtha, is mentioned without a word of protest. We have often wondered who devised this unhappy expedient.

Many readers will be surprised at the statement that gin is obtained from potatoes. Unless some recent change has been made this popular spirit, both in Holland and England, is obtained from grain, in company with juniper berries. A very vile whisky, rich in fusel, is distilled from potatoes in north-eastern Germany. It is an edifying sight to see a Pomeranian peasant take a glass of this spirit, and fling it down his throat with a shudder.

Caffeine and theobromine are merely mentioned in passing.

A striking feature of the work is an Appendix of ten pages, consisting of questions taken ftom the examination papers of the Science and Art Department, and of the University of London

Our opinion is that the author could produce a more valuable work had he not the fear of the Department ever before his eyes.

The Extra Pharmacopœia. By William Martindale, F.C.S., late Teacher of Pharmacy and Demonstrator of Materia Medica at University College. *Medical References and a Therapeutic Index of Diseases and Symptoms.* By W. Wynn Westcott, M.B. Eighth Edition. London: H. K. Lewis. 1895.

The fact that this manual has now reached its eighth edition is sufficient proof that it is duly appreciated by the medical profession and by the pharmacists.

In addition to many minor novelties, we must particularly notice a section on antitoxins, serums, and lymphs. These substances are alternated morbid products, which in some cases, if injected into the tissues of a man or other animal, exert a curative or even an immunifying effect. Of these agents, excepting vaccine, the oldest and best known is Pasteur's antitoxin for rabies. The death-rate among persons bitten, without this treatment was about two hundred per thousand, whilst by means of Pasteur's treatment it is reduced to from two to three per thousand. The treatment for tetanus, devised by Cattani and Tizzoni, is still *sub judice.* If thoroughly established it will be of immense value to the army in India, where wounds, even if trifling, are often followed by fatal tetanus.

The balance of results seems unfavourable as regards Koch's tuberculin. The antitoxin for diphtheria appears to have been more successful. We must not forget that all remedial agents of this type are strenuously denounced by the "Anti-vaccinationists." They have vehemently opposed the formation of the British Institute of Preventive Medicine.

It is painfully interesting to notice how the use of arsenical cosmetics—the so-called Styrian vice—is spreading in Britain. We do not, of course, find any such preparations recommended in the work before us, but they are being increasingly advertised, and of some of them it is said that they are inventions of doctors.

CORRESPONDENCE.

THE ATOMIC WEIGHT OF YTTRIUM.

To the Editor of the Chemical News.

Sir,—I read with interest Mr. Jones's paper on the atomic weight of yttrium (Chemical News, lxxi., p. 170). That paper suggests to me a few remarks, which I beg leave to submit to the reader. The bearing of the chemistry of the rare earths on the periodic law gives to their metals an importance which they otherwise would not be entitled to.

It is necessary for my purpose to complete the history of the determination of the atomic weight of yttrium. Mr. Jones does not seem to be acquainted with the following facts:—

In February, 1866, I published four determinations of the atomic weight of yttrium, giving an average of 87·7.

M. Berlin, of Stockholm, found from 87 to 87·3 for the same metal.

In his "Elements of Chemistry" M. Mendeleeff says that he found 87·9 in 1871.

My yttria and that used by Mr. Berlin were white.

Prof. Clève's results, published later, are somewhat higher (89·7), but his yttria was pale yellow.

Moreover, the history of the question shows that the nearer to purity the paler yttria is, and the lower its molecular weight. From an yttria corresponding to 89·7 I readily separated a more coloured earth. Berzelius, Scherer, Mosander, Marignac, and Crookes, all agree that yttria is white.

Although evidently inaccurate, Prof. Clève's results are adopted by all chemists, probably on account of the reputation of the Upsala *savant* and in order to meet the requirements of the periodic law.

Now I come to the point. Working on a scandia free yttrium oxide, I find my results of 1866 correct. Thus Mr. Jones, M. Berlin, and myself, experimenting on white yttria, have obtained results the divergence of which can hardly be accounted for on the ground of experimental errors :—

Jones	89
Delafontaine ..	87·7 (87·3 now)
Berlin	87·3.

We are then led to suppose that yttria without any admixture of scandia is not a homogeneous compound. This is what I am trying to find out, and why I do not publish now my recent numerical results. As is well known, Mr. Crookes discovered, several years ago, a number of facts raising the same question.

The fact that the periodic law requires Y = 89, instead of any lower figure, has not in my mind as much weight as with other chemists. Having worked, and being still working, on large quantities of materials extracted from samarskite, fergusonite, euxenite, polycrase, and gadolinite, I have come to the conclusion that the atomic weight of scandium is lower than 44, If the periodic law absolutely requires 44, then scandium is not ekaboron. Philippium, denied by some eminent chemists, is nevertheless well characterised chemically, and its spectrum contains lines not belonging to yttrium and terbium.

Chemists with a sufficient supply of raw material will find that the old didymium oxide is a mixture of at least four compounds—praseo-didymium, neodidymium, samarium oxide, and another forming dichroic purplish salts.

Gadolinium is identical with decipium, and disappears from the list.—I am, &c.,

P. Delafontaine.

South Division High School,
Chicago, April 27, 1895.

ATOMIC WEIGHTS.

To the Editor of the Chemical News.

Sir,—Although it might be urged that until we know more about helium and argon, and the elemental gases probably associated with them, it would be well to cease speculation concerning the Periodic Law, I do not think that any harm can be done by pointing out certain interesting relationships between the magnitudes of the atomic weights of the elements.

I therefore venture to call attention to an arrangement of the elements, according to their atomic weights and valencies, which not only indicates that there are probably some missing elements, but also enables their atomic weights to be roughly calculated.

In the first column of the accompanying Table the elements having odd valencies are entered in the order of their atomic weights. Between Nb and Rh space is left for an element predicted by Mendeleeff. Against them in col. 2 are given their atomic weights, and in col. 3 the differences between consecutive atomic weights.

In col. 7 are entered the elements having even valencies. Be is not entered on a line with H, but on a line with B, which it immediately precedes on the atomic scale. Similarly C is on a line with N, which it also immediately precedes. And so on with the other elements having even valencies. In col. 6 are entered their atomic weights, and in col. 5 the differences between consecutive atomic weights.

Atomic Weights of Elements.

Perissads.					Artiads.	
Element. 1.	At. wt. 2.	Differences. 3.	4.	5.	At. wt. 6.	Element. 7.
H	1·00				0·00	—
		6·02	−1·02	5·00		
Li	7·02				5·00	?
		3·98	+0·12	4·10		
B	11·00				9·10	Be
		3·03	−0·13	2·90		
N	14·03				12·00	C
		4·97	−0·97	4·00		
F	19·00				16·00	O
		4·04	−0·04	4·00		
Na	23·04				20·00	?
		3·97	+0·33	4·30		
Al	27·01				24·30	Mg
		4·02	+0·01	4·03		
P	31·03				28·33	Si
		4·43	−0·70	3·73		
Cl	35·46				32·06	S
		3·68	+0·26	3·94		
K	39·14				36·00	?
		4·96	−0·88	4·08		
Sc	44·10				40·08	Ca
		7·30	+0·75	8·05		
V	51·40				48·13	Ti
		3·60	+0·57	4·17		
Mn	55·00				52·30	Cr
		3·70	+0·02	3·72		
Ni	58·70				56·02	Fe
		4·70	−1·36	3·34		
Cu	63·40				59·36	Co
		6·50	−0·56	5·94		
Ga	69·90				65·30	Zn
		5·19	+1·81	7·00		
As	75·09				72·30	Ge
		4·86	+1·94	6·70		
Br	79·95				79·00	Se
		5·55	−1·55	4·00		
Rb	85·50				83·00	?
		3·50	+1·00	4·50		
Y	89·00				87·50	Sr
		5·00	−2·50	2·50		
Nb	94·00				90·00	Zr
		4·50	+1·20	5·70		
?	98·50				95·70	Mo
		4·50	+1·45	5·95		
Rh	103·00				101·65	Ru
		4·93	−0·23	4·70		
Ag	107·93				106·35	Pd
		5·77	−0·02	5·75		
In	113·70				112·10	Cd
		6·60	+0·40	7·00		
Sb	120·30				119·10	Sn
		6·55	−0·65	5·90		
I	126·85				125·00	Te

Omitting the first line the vacant spaces are regarded as indications that elements may be found to fill them. Such elements fall between H and Li, F and Na, Cl and K, Br and Rb, and so on with increasing atomic weight. Their atomic weights are roughly 5, 20, 36, 83, &c.

In col. 4 are given the differences between cols. 3 and 5. The agreement, it will be seen, is fairly good, large and small values in cols. 3 and 5 alternating in unison.

Any additional elements put in, even if they did not produce greater discrepancies than col. 4 now shows, would interfere with the regular increase and decrease in valency.

Elements of greater atomic weight than iodine have not been put in the table, as their atomic weights are in some cases uncertain, and the figures throw no additional light upon the subject.—I am, &c.,

R. M. Deeley.

10, Charnwood St., Derby.

ACTION OF HYDROGEN GAS ON AMORPHOUS PHOSPHORUS.

To the Editor of the Chemical News.

Sir,—It would interest me, and probably others, to know if any of your readers have repeated an experiment recently described in the Chemical News, namely, the direct combination of hydrogen with amorphous phosphorus to form phosphine.

My attempts have not proved successful. In the first experiment some amorphous phosphorus was heated in a tube through which hydrogen was passing, and the gas, after traversing a wash-bottle containing water, was led to a pneumatic trough. A gas escaped which fumed in the air, but did not spontaneously inflame, the fuming appearing to be due to the presence of finely-divided phosphorus carried over mechanically.

In the second experiment a piece of combustion-tube was bent at right angles, and some amorphous phosphorus was placed in the horizontal part of the tube, whilst the vertical limb dipped into mercury. Hydrogen was passed over the phosphorus, which was heated until about half of it had been transformed into the ordinary modification; the gas was then passed until the tube cooled, and the hydrogen apparatus was sealed off. On heating the amorphous phosphorus in the hydrogen no diminution of volume was observed.

In the third experiment dried hydrogen was passed over amorphous phosphorus which had been washed with water until neutral and then dried. The phosphorus was first gently heated, just sufficiently to change it to the ordinary variety, and later the tube was raised to a higher temperature. The resulting gas was passed through a wash-bottle containing water, and then through a U-tube filled with wet glass beads to remove suspended phosphorus, and finally into a solution of cupric sulphate; but no precipitate of phosphide of copper resulted.

It is probable that I have not worked under exactly the proper conditions, and I should be obliged to any one who has been more fortunate than myself if he will give me the benefit of his experience.—I am, &c.,

Herbert McLeod.

Cooper's Hill, Staines,
May 13, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 17, April 29, 1895.

New Researches on the Combining Heats of Mercury with Elements. — Raoul Varet.—This thermochemical memoir does not admit of useful abstraction.

Researches on Manganese.—Charles Lepierre.—The author, continuing the study of the action of fused ammonium sulphate, or better bisulphate, upon metallic salts, shows the results obtained with manganese. On adding to ammonium sulphate about one-fifth of its weight of crystalline manganese sulphate there is obtained, after the expulsion of the water of crystallisation (180°—200^{c}), a deposit of large crystals of the cubic system, which after decanting off the excess of the ammoniacal salt and purification with boiling alcohol at 70 per cent, corresponds to the formula $2SO_4MnSO_4.Am_2SO_4Mn$. On heating this anhydrous salt either alone or in the liquid in which it has been formed it is converted at 350° into anhydrous manganous salt. This salt is very hygroscopic; sp. gr. at 12° is 3·14. Hence manganese behaves like nickel and cobalt and does not, like iron, form super-oxygenated salts. The author has obtained an alum, anhydrous ammonium manganic $(SO_4)3Mn_2.SO_4Am_2$.

Campholenic Amides and Acids.—A. Béhal.—The author has examined the three amides fusible respectively at 86°, 130·5°, and 106°. He concludes that the amide fusible at 106° is a molecular compound of the amides fusible at 86° and 130·5°.

Double Compounds of Anhydrous Aluminium Chloride with Nitro-compounds of the Aromatic Series.—G. Perrier.—The author, referring to the researches of Stockhausen and Gattermann, states that he has found that most of the compounds belonging to the various functions of organic chemistry combine with aluminium chloride. Among those experimented on are nitrobenzene, paranitrotoluene, nitronaphthaleine-α, dinitrobenzene (meta and 1.2.3), and paranitranisol.

On an Error which may Occur by the Use of Fehling's Liquid in the Detection of Sugar in the Urine of Persons under Treatment with Sulphonal.—Ph. Lafon.—Fehling's solution in such cases may give a strong yellow precipitate, though the same urine if examined with the polari-saccharimeter under yellow monochromatic light gives no dextro-deflection, the characteristic of dia betic sugar, but a faint deflection to the left.

Panification of Brown Bread.—James Chappuis.—This is the opening of a "*pli cacheté.*" The bread in question is the result of the action of a diastase, cerealine, of Megé Mouriès upon the paste. The diastase of wheat (and probably of other grain) is destroyed by oxygenated water. It is possible to make white bread with flour of all qualities.

Causes which Produce the Colour of Brown Bread.—Léon Boutroux.—Gluten can give colour to bread on desiccation but not on fermentation. Bran may give colour to bread by the action of atmospheric oxygen in presence of water, but not by fermentation. The acidity of yeast, far from being to be feared in this respect, is a protection against browning.

Zeitschrift für Anorganische Chemie,
Vol. vii., Part 6.

Transformation of Black Mercury Sulphide into the Red Form, and on the Density and Specific Heat of both Substances.—W. Spring.—The elasticity of solids is only perfect in cases where the presence of allotropic modifications is excluded. Otherwise the substance assumes a denser state, corresponding to the decrease of volume to which they have been subjected. It appears that for solids as well as for gases there is a critical point, above or beneath which an increased pressure occasions no change in the condition of the substance. The black modification of mercury sulphide must undergo a decrease of volume in order to pass into the red state. This explains a number of observations made upon mercury sulphide. If the black sulphide is vigorously rubbed in an agate mortar we see a red streak where the pestle has acted. A temperature of 410° is the critical-point above which the red modification cannot exist.

Preservation of Chemically Pure Alkaline Solutions.—Alexander von Kalecsinsky.—The author fits into a straight-sided flask a beaker of sheet silver or platinum, so that a small place is left at the sides and the bottom between the metal and the glass. A silver or platinum tube passes through the stopper to near the bottom. A glass tube also passes through the stopper but does not dip into the liquid. On blowing into this latter tube the alkaline liquid ascends out of the metal pipe, and can be allowed to escape for use.

Some Methods for Separating Phosphoric Acid as an Alkaline Phosphate from the Calcium and Ferric Phosphates.—E. A. Schneider.—The author indicates a process which resolves itself into three phases:—A. The phosphorite is opened up with sulphuric acid, which must be in greater excess when the proportion of ferric oxide is small. In this case the excess of sulphuric acid is saturated with ferric hydroxide, which is obtained as a by-product in the further course of the process. The solutions must be kept very concentrated. B. The solution of ferric phosphate in ferric sulphate obtained in this manner is mixed with a sufficiency of water to throw down a considerable quantity of ferric phosphate. Complete precipitation would be disadvantageous, on account of the large quantity of water needful. The mother liquors are mixed with fresh portions of the crude material with the addition of more sulphuric acid. In case of ground basic slags, the solution must be more concentrated than for other materials, on account of the more abundant formation of crystallised gypsum. C. The ferric phosphate is decomposed with potassa-lye. In view of the improved electric process for the production of potassium hydroxide, its employment does not seem to be excluded. If an apparatus for dialysis should work successfully on the large scale, the ammoniacal solution of the ferric phosphate might be dialysed up to the point when the diffusion of the ammonium phosphate ceases, and the undecomposed ferric phosphate might be treated with potassa-lye.

Complex Inorganic Acids.—F. Kehrmann.

Phosphoduodecimolybdic Acid and Phospholuteomolybdic Acid.—(Experiments by E. Bohm).—The results, showing the action of the acids with the saline solutions of metals and organic bases, are given in the form of three tables.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Tests for Morphine in Urea.—Will some correspondent kindly intimate the best source for obtaining information as to the most delicate tests for morphine in urea.—A. R. P.

MEETINGS FOR THE WEEK.

Monday, 20th.—Society of Arts, 8. (Cantor Lectures). "Japanese Art Industries," by Ernest Hart, D.C.L.
— Medical, 8.30. (Annual Oration).
Tuesday, 21st.—Royal Institution, 3. "Thirty Years' Progress in Biological Science," by Prof. E. Ray Lankester, F.R.S.
— Institute of Civil Engineers, 8.
— Pathological, 8.30. (Anniversary).
— Society of Arts, 8. "Commercial Education in Belgium," by Prof. William Layton.
Wednesday, 22nd.—Society of Arts, 8. "The Dressing and Metallurgical Treatment of Nickel Ores," by A. G. Charleton, A.R.S.M.
— Geological, 8.
Thursday, 23rd.—Royal Institution, 3. "The Instruments and Methods of Spectroscopic Astronomy," by William Huggins, D.C.L., F.R.S.
— Society of Arts, 4.30. "The Northern Balochis—their Customs and Folklore," by Oswald V. Yates.
— Institute of Electrical Engineers, 8.
Friday, 24th.—Royal Institution, 9. "The Absolute Measurement of Electrical Resistance," by J. Viriamu Jones, F.R.S.
— Physical, 5. "On Mixtures of Ethane and Nitrous Oxide," by Dr. Kuenen. "The Measurement of Cyclically varying Temperature," by H. F. W. Burstall.
Saturday, 25th.—Royal Institution, 3. "Picture Making," by Seymour Lucas, A.R.A.

THE CHEMICAL NEWS.
Vol. LXXI., No. 1852.

FORMIC ALDEHYD: ITS DETECTION IN MILK, AND VALUE AS A PRESERVATIVE.

By R. T. THOMSON, F.I.C.

The commercial form of this article, known as formalin, may be obtained for chemical purposes as a liquid guaranteed to contain 40 per cent of real formic aldehyd; but a much weaker solution appears to be sold to some extent to milk dealers for adding as a preservative to milk, in place of boric acid or borax.

As formic aldehyd requires to be added to milk only in very small quantity, it is evident that its detection, and especially its estimation, presents unusual difficulties. I have recently made experiments with the object of proving the presence of this substance in milks, and have found that a modification of the well-known reaction with ammonia-nitrate of silver gives a good indication of its presence. To apply the test 100 c.c. of the milk are carefully distilled until (say) 20 c.c. of distillate comes over: this is transferred to a stoppered tube, and about 5 drops of ammonia silver nitrate added. (This solution is prepared by dissolving 1 grm. of silver nitrate crystals in 30 c.c. of distilled water, adding dilute ammonia till the precipitate at first formed is re-dissolved, and then making up to 50 c.c. with water). The mixture of the milk distillate and the silver solution is now allowed to stand for several hours in a dark place (as much as twelve to eighteen hours may be necessary if very little formic aldehyd is present), when, if formic aldehyd is present, a strong black colour or deposit will be produced. A light brown colour should be disregarded; but, so far as my experience goes, the production of a decided black under these circumstances is only brought out by formic aldehyd, but possibly by other aldehyds also. The usual method of heating with the silver solution in order to obtain a silver mirror is of no value with weak solutions of formic aldehyd. It was found that genuine milks from various sources, when tested by the method described, gave no reaction whatever, even when the distillate was left mixed with the silver solution for twenty-four hours; or at most gave a slight brown tinge. When as little as 2 grains of the 40 per cent formalin was added to 1 gallon of milk (which before addition gave no reaction with this process), the distillate from 100 c.c. gave a decided black colour, or deposit intense enough to render the mixture quite opaque. As 2 grains per gallon is a quantity of formalin which would be of little value in the preservation of milk, it is evident that this method of testing is quite delicate enough for the purpose. It ought to be noted that, if a milk contains about 2 grains of formalin per gallon, the 20 c.c. distillate from 100 c.c. of the milk appears to contain all the formic aldehyd that will distil over, and distillates after that give practically no reaction. A milk containing 7 or 8 grains per gallon of the preservative may require the distillation to be carried on till 30 or 40 c.c. are collected, before it ceases to show a reaction with the silver solution; but in all cases the reaction can be got by distilling over the 20 c.c., or indeed 10 c.c.

An attempt was made to determine the proportion of formic aldehyd in a milk by comparing the depth of colour obtained from its distillate with that given by a standard solution of the aldehyd. This was not successful, owing to the fact that the reduced silver often forms a deposit on the side of the tube, while the liquid is comparatively colourless. In this connection it was noticed that the distillate from a milk containing a certain proportion of formic aldehyd did not give nearly so great a depth of black colour as the same amount simply added to water, and then tested with the silver solution. This would point to the conclusion that there is a loss of formic aldehyd, probably by decomposition, during the distillation, and this also would add to the incorrectness of a determination.

I should have mentioned that care should be taken not to add excess of ammonia to the ammonia silver nitrate solution used in the test, as if much excess of ammonia is present no reaction will be obtained, even in presence of formic aldehyd.

It has been mentioned by other chemists that formalin may be used as a preservative for milk samples; and I have found by experiment that samples, to which has been added 4 or 5 drops of the 40 per cent formic aldehyd per 100 c. c. of the milk, have kept in good condition for six weeks, and given the same results, on analysis after that period, as when analysed before the preservative was added. As formic aldehyd is in such an available form for addition to milk samples, without in any way interfering with the accuracy of the results of analysis, it should prove useful to analysts in the preservation of samples for reference. As in the case of other preservatives, its use for milk supplies should not be recommended until its harmlessness were fully proved.

I have also made a few experiments with the view of comparing the value of formic aldehyd as a preservative with such well-known articles as boric acid, salicylic acid, and benzoic acid. For this purpose measured quantities of the same milk, to which the various preservatives were added, were kept in stoppered bottles under the same conditions as nearly as possible, and the condition of each examined from time to time, one sample of the milk free from preservative being also kept along with these for comparison. In the following Table will be found the results of the observations made:—

Table showing the Preserving Power, as regards Milk, of Certain Preservatives.

Preservative employed.	Milk after standing 6 days.	Milk after standing 7 days.	Milk after standing 8 days. Lactic acid per cent.	Milk after standing 11 days. Lactic acid per cent.
None	Sour	Sour, curdled	0·68	0·71
40 p.c. formic aldehyd (8¾ grs. per gall.)	Sweet	Sweet	0·12	0·43
40 p.c. formic aldehyd (17½ grs. per gall.)	Sweet	Sweet	0·10	0·14
40 p.c. formic aldehyd (35 grs. per gall.)	Sweet	Sweet	0·07	0·10
Boric acid (35 grs. per gall.).. ..	Turned	Sour, curdled	0·42	0·52
Boric acid and borax in equivalent quantities (= 35 grains boric acid)	Sweet	Sweet	0·10	0·32
Salicylic acid (35 grs. per gall.)	Sweet	Sweet	0·10	0·33
Benzoic acid (17½ grs. per gall...	Slightly turned	Sour	0·45	0·52

It is apparent from these results that 8¾ grains of the 40 per cent solution of formalin are quite as effective in preserving milk as four times that amount of boric acid (at least when used as a mixture of boric acid and borax), and the same proportion of salicylic acid, while the preserving power of benzoic acid is very low compared with what might be expected from statements made in text-books. It also seems peculiar that boric acid alone is much inferior to a mixture of boric acid and borax, so made up that each of these substances contributes equal to 17·5 grains of crystallised boric acid per gallon of milk. The proportion of 35 grains of boric acid per gallon of milk was adopted because that is about the usual amount I have found in samples to which that preservative had been added.

It may quite reasonably be argued that the results given above are not sufficient in number to allow of any decided opinion as to the exact comparative value of the preservatives tested; but, taking into consideration the concordant results of the three tests with formic aldehyd, I have no hesitation in claiming that these are approximately the values of the respective preservatives for milk at least.

I am continuing my experiments with formic aldehyd, in order to find a method of determining the amount present in a milk, as well as its value in preserving milk samples, and also further and extended experiments on the value of the various preservatives.

City Analysts' Laboratory, Glasgow.

SODIUM BISULPHITE.

By R. E. EVANS and C. H. DESCH.

During the severe weather experienced during the early part of this year a great number of compounds crystallised out from solutions which at ordinary temperatures have no tendency in this direction. The following account of a compound obtained in this manner may be of interest, as it has not been previously described.

A quantity of about 95 gallons of bisulphite of soda solution, of sp. gr. 1290, was left exposed for several days during the most severe frost, and on running off the liquid the sides of the vat were found to be incrusted with large glittering crystals, the total quantity of which must have exceeded 2 cwt. They were very regular in shape, and, exposed to the air, tended to effloresce with a faint smell of sulphurous acid.

Analysis gave the following results:—

	Crystals.	Calculated for $Na_2SO_3SO_2+7H_2O$.
Na_2O	20·01	19·56
SO_2	39·81	40·50
Na_2SO_3	40·66	39·87
SO_2	19·16	20·26
H_2O	40·18	39·87

The compound was therefore crystallised bisulphite of soda, with 7 molecules of water of crystallisation. A considerable quantity of the crystals were stored in a well-stoppered bottle, but in a short time, as the weather became warmer, they partly deliquesced, forming a semifluid mass, consisting of fine pearly white crystals suspended in a heavy fluid. These were filtered off, and drained as far as possible by pressure between filter-paper. They gave off SO_2 rather strongly, and the analysis was therefore performed at once, and the remaining moisture (2·5 per cent) was allowed for in the calculations:—

	Crystals.	Calculated for $Na_2SO_3SO_2$.
Na_2O	32·74	32·63
SO_2	67·26	67·37
Na_2SO_3	66·37	66·31
SO_2..	33·63	33·69

There can be no doubt, therefore, that this salt was anhydrous bisulphite of soda. The gravity of the liquid portion was 1164·98, and consisted of a solution of the bisulphite,

It is evident, therefore, that by intense cold a very well-crystallised form of bisulphite of sodium may be obtained containing 7 molecules of water; and this is readily given up, even in a closed space, with formation of the more stable bisulphite.

The Laboratory, Stratford-on-Avon.

ARGON IN MINERALS.

We have received a letter from Professor W. R. Eaton Hodgkinson from which we extract the following interesting observations:—

"I have obtained from certain minerals gases which seem to contain argon, and perhaps also helium. Minerals of the samarskite group when heated to some particular temperature commence to glow, and this appearance has hitherto been ascribed to a molecular rearrangement. As I could not find any account as to whether the weight was in any way changed in this action, I have recently, with my assistant, Mr. Young, A.R.S.M., heated euxenite and samarskite *in vacuo* and extracted the gases. At the moment of glow a large quantity of gas—twelve times the volume of the mineral —is given off. This gas we have sparked, and the colour and spectrum point to a hydrocarbon being present. On adding oxygen to the gas and exploding, there is a decided contraction, and after introducing potash a further greater contraction. After the excess of oxygen is absorbed the spectrum is no longer like a hydrocarbon, but has a close resemblance to the argon spectrum, according to the published accounts. We have so far obtained the same results from euxenite as from samarskite."

ON THE PHOTOGRAPHY OF THE RAYS OF SMALLEST WAVE-LENGTH.*

By VICTOR SCHUMANN.

Previous experiments which I had performed with strata of air up to 1 m.m. in thickness had shown that the photography of the light rays below the wave-length 185 $\mu\mu$ required the exclusion of air from the track of the rays. Under these circumstances, an essential extension of the spectrum of the air beyond the wave-length 185 $\mu\mu$ seemed impracticable. But, according to my most recent experiments, very thin strata of air, such of about 0·1 $\mu\mu$ in thickness, transmit a great part of the rays of the smallest wave-lengths, and strata whose thickness does not exceed a few hundredths of a m.m. seem merely to check, but not to quench, the energy of the rays. With the former the photograph extends far beyond 162 $\mu\mu$, the locality of the photographic maximum of hydrogen; whilst with the latter we are able to proceed considerably further. Indeed, according to all appearance, these, if only exposed for a sufficient time, may present no important hindrance to attaining the actual limit of the region of the smallest wave-lengths.

From this fact, which I have repeatedly verified, I believe that I can deduce a result concerning the photography of the smallest wave-lengths totally unexpected in accordance with my earlier observations. I employ a discharging tube, so constructed that it may be connected air-tight with the exhausted spectrograph in a manner suitable for photographic application, and thereupon, independently of its vacuum, can be filled with any required gas at any given pressure. The tube and the spectrograph, therefore,—in an essential contrast with my former experimental arrangement—were not in conductive connection. This discharging-tube, differing in form and arrangement from my previous arrangements of this kind, presents, along with other advantages, one which comes exclusively into consideration in the present case, *i.e.*, that the resistance of absorption which the rays encounter by the contained gas can be reduced without difficulty to an extremely small quantity by a decrease of pressure and depth of stratum.

I purpose subsequently to communicate further par-

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* Imperial Academy of Sciences at Vienna, Session of the Class of Mathematics and Natural Science, April 25, 1895.

ticulars with my photographs—now in course of execution—of the ultra-violet spectrum of hydrogen.

With such a tube I now obtained, after it has been filled with dry air at a low pressure, the spectrum of the air as an extremely energetic band of efficacy, of a wave-length hitherto not attained, which closely approximates, in photographic energy and extent, to the most effective of all the ultra-violet spectra hitherto known, that of hydrogen. For instance, the most effective region of these pictures presents in a length of 34 m.m. more than fifty bands, partly resolved into lines shading away towards the red, and following upon each other so closely that in their totality they appear to the naked eye as a continuous effective band of varying density. To what constituent of the atmosphere these bands belong future observations must decide.

VARIATION IN THE AMOUNT OF FREE AND ALBUMENOID AMMONIA IN WATERS, ON KEEPING.

By A. LIVERSIDGE, M.A., F.R.S.,
Professor of Chemistry, University of Sydney, N.S.W.

(Concluded from p. 237).

Table VII.

About 1 grm. of White of Egg was diffused as uniformly as possible, first through a small quantity and then through a larger volume of Distilled Water, and nine quart bottles filled up with the mixture.

Temp. °F. Morn.	Temp. °F. Even.	Nos.	Date.	Free NH_3.	Alb. NH_3.
72	72	1	Nov. 24	0·33	0·37
66	69	2	,, 27	0·33	0·49
66	68	3	,, 29	0·50	0·56
67	68	4	,, 30	0·40	0·60
68	68	5	Dec. 1	0·40	0·70
66	71	6	,, 4	0·60	0·70
73	73	7	,, 6	0·60	0·77
76	77	8	,, 7	0·60	0·72
77	78	9	,, 8	0·50	0·80

It will be noticed in the above table that the amounts of both free and albumenoid ammonia increased very greatly after four or five days, showing that the fresh albumen, like urine, does not yield ammonia so readily as that which is more or less decomposed; as the amount of albumenoid ammonia had increased in the ninth and last bottle, a larger series would have been more satisfactory.

Table VIII.

Eight Bottles each of Garden Tank Water and NH_4NO_3 and Distilled Water and NH_4NO_3.

(Rained heavily for 24 hours before putting up this series).

Temp. °F. Morn.	Temp. °F. Ev.	Nos.	Date.	Garden Tank Water and NH_4NO_3. Free NH_3.	Garden Tank Water and NH_4NO_3. Alb. NH_3.	Distilled Water and NH_4NO_3. Free NH_3.	Distilled Water and NH_4NO_3. Alb. NH_3.
75	76	1	Nov. 17	0·46	0·09	0·40	0·09
75	76	2	,, 23	0·36	0·05	0·32	0·05
66	69	3	,, 27	0·04	0·05	0·30	0·09
68	69	4	,, 28	0·03	0·04	0·48	0·11
66	68	5	,, 29	0·03	0·04	0·48	0·07
67	68	6	,, 30	0·03	0·04	0·40	0·11
68	68	7	Dec. 1	0·03	0·04	0·48	0·11
66	71	8	,, 4	0·02	0·04	0·50	0·09

It will be noticed that the distilled water containing ammonium nitrate yielded nearly equal amounts of free and albumenoid ammonia all through the series, but the mixture of ammonium nitrate and garden tank water soon showed a rapid diminution in the amount of ammonia. The great change which had taken place was probably due to the fermentation or decomposition of organic matter in the tank water or to the action of organisms, or perhaps to both. The amounts of albumenoid ammonia were small throughout, but larger than those yielded by the other series of garden tank water.

Table IX.

Ten Bottles each of Horse Pond and Fish Pond Waters, undiluted.

Temp. °F. Morn.	Temp. °F. Ev.	Nos.	Date.	Horse Pond. Free NH_3.	Horse Pond. Alb. NH_3.	Fish Pond. Free NH_3.	Fish Pond. Alb. NH_3.
73	75	1	Dec. 11	10·00	7·00	0·12	0·90
77	78	2	,, 12	2·00	2·00	0·11	0·92
71·5	73	3	,, 13	8·00	4·00	0·16	1·04
76	78	4	,, 15	7·00	4·00	0·16	1·03
80	78	5	,, 16	6·00	2·00	0·38	0·69
74	75	6	,, 19	5·00	2·00	0·52	0·56
76	77	7	,, 20	4·00	1·00	0·70	0·38
75	76	8	,, 21	2·00	0·50	0·90	0·30
			1877.				
75	75	9	Jan. 8	0·50	0·25	1·38	0·06
73	74	10	,, 10	0·07	0·07	1·50	0·04

Note.—On account of the large quantity of organic matter present in the horse pond water, 10 c.c. only of it was used for each determination; this was made up in the retort to 500 c.c. by the addition of distilled water free from ammonia.

Table X.

Seven Bottles each Garden Tank and Peaty Water and Garden Tank and Ammonia Solution.

Temp. °F. Morn.	Temp. °F. Ev.	Nos.	Date.	Garden Tank and Peaty matter. Free NH_3.	Garden Tank and Peaty matter. Alb. NH_3.	Garden Tank and Free NH_3. Free NH_3.	Garden Tank and Free NH_3. Alb. NH_3.
73	75	1	Dec. 11	0·72	0·19	2·8	0·20
77	78	2	,, 12	1·12	0·04	2·80	0·20
71·5	73	3	,, 13	1·12	0·13	2·72	0·23
76	78	4	,, 15	1·08	0·12	2·70	0·21
80	78	5	,, 16	0·03	0·04	0·64	0·10
74	75	6	,, 19	0·02	0·03	0·56	0·07
76	77	7	,, 20	0·01	0·01	0·20	0·01

The self purification of the above samples is very remarkable.

DETECTION AND ESTIMATION OF SELENIUM IN METEORIC IRON.

By H. N. WARREN, Research Analyst.

The following is an outline of the analysis of several specimens of meteoric iron which have been lately brought before my notice, and which, during the course of analysis, were all more or less found to contain small quantities of selenium associated with the iron, the separation of which was effected as follows:—

By reducing 10 grms. of the specimen to a rough powder by filing, and intimately mixing it with pure flour of sulphur in sufficiency, the whole being introduced into a stout piece of combustion tubing and heated to redness. One end of the tube is in connection with an apparatus evolving oxygen gas, for the purpose of burning off the sulphur, forming sulphurous anhydride, and expelling with it the small quantity of selenious anhydride formed at the same time by the combustion of the selenium present. The further end is connected with a series of bulb tubes containing distilled water to collect the reduced selenium formed by the action of the sulphurous acid produced. The solution containing the precipitated selenium is next

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* Read before the Australasian Association for the Advancement of Science, Brisbane, January, 1895.

heated to a temperature of 80° F., to render it more dense, introduced into a platinum dish, dried in the air-bath, and weighed (a blank estimation being in each case determined with the sulphur employed). A tabulated view is appended of the meteoric iron whem separated from the matrix. A, B, from Bohumilitz; C, Pallus iron; D, Elbogen; E, F, Atacama Desert.

	A.	B.	C.	D.	E.	F.
Iron	90·10	94·51	95·04	88·20	70·01	86·52
Nickel . ..	6·54	2·54	3·20	8·20	20·02	10·52
Cobalt . ..	0·24	0·32	0·12	0·12	—	0·12
Copper ..	—	—	0·20	—	—	—
Manganese.	0·12	—	0·12	0·23	—	—
Selenium ..	0·23	0·050	0·04	0·06	0·08	0·05

Liverpool Research Laboratory,
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LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, May 8th, 1895.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined two were recorded as "clear but dull," the remainder were clear, bright, and well filtered.

The London waters have now assumed the high degree of purity which we are accustomed to observe during the summer when the activity of fluviatile vegetation, unduly kept back during the abnormally low temperature of the last few months, is fully at work, oxidising and transforming the dissolved organic matter and lowering the colour. In chemical composition the analyses show almost the same results as were obtained last month, a slight improvement being seen in common salt, hardness, nitric acid, and colour.

Bacteriologically the filtered waters from the general wells at the works contained an average of 46 microbes per c.c., while the unfiltered water contained 9175 per c.c., showing a filtration efficiency of 99·5 per cent.

The rainfall at Oxford has been identical with the average for 25 years, being in each case 1·78 inches. Of this amount more than one-third fell on the 25th inst.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

A NEW CLASS OF COMPOUNDS OF THE INACTIVE HYDROCARBONS.

No. II.

By J. ALFRED WANKLYN and W. J. COOPER.

IN the CHEMICAL NEWS (vol. lxx., p. 211) we published a note with the above title, explaining that the thermal phenomena attendant on the mixture of the hydrocarbons of Russian kerosene with glacial acetic acid point to the conclusion that these hydrocarbons enter into chemical combination with acetic acid.

We have continued the investigation, which bears out this conclusion most completely.

In the first place it has become quite clear that one molecule of each hydrocarbon enters into chemical combination with one molecule of the fatty acid, forming a liquid compound endowed with sufficient stability to admit of its being purified and handled, and analysed in a thoroughly satisfactory manner. We have obtained the acetic combination with each one of seven consecutive terms of the kerosene series, the analyses of which we give:—

		Percentage of Hydrocarbon.	
		Theory.	Found.
xiv.	*$C_{14}H_{14},C_4H_4O_2$	62·04	62·33
xv.	$C_{15}H_{15},C_4H_4O_2$	63·63	62·75
xvi.	$C_{16}H_{16},C_4H_4O_2$	65·12	64·48
xvii.	$C_{17}H_{17},C_4H_4O_2$	66·48	65·9 (mean)
xviii.	$C_{18}H_{18},C_4H_4O_2$	67·74	67·85
xix.	$C_{19}H_{19},C_4H_4O_2$	68·91	69·06
xx.	$C_{20}H_{20},C_4H_4O_2$	70·00	69·70

The analyses were made by taking advantage of the circumstance that all of these acetic combinations with the hydrocarbons are readily decomposed by water. A comparatively large quantity of the acetic compound was employed—from 30 to 120 grms.: this was treated with water and washed thoroughly, and the resulting oily hydrocarbon was weighed. The results, as will be seen, are perfectly satisfactory.

The preparation of the compounds is very simple, and, with one exception, the compound is very readily obtained in a fairly pure condition.

The hydrocarbon is mixed with a moderate excess of glacial acetic acid, and, when necessary, gently warmed. Two layers of liquid are formed, the upper and larger layer being the compound which is sought, and the lower being acetic acid holding some of the acetic compound in solution. A glass stop-funnel is used in order to separate the two layers of liquid. Instead of taking only a moderate excess of the acid, a large excess—that is to say, more than twice the theoretical quantity of acid—may be taken. In that case the addition of a minute quantity of water, amounting to about 0·1 c.c. to 25 c.c. of the acid, may be resorted to in order to remove the excess of acetic acid. A similar result is arrived at by adding a very small quantity of formic acid.

As has been said, we have experienced no difficulty in preparing six of the seven acetic compounds the formulæ of which have been set out. The exception is the compound of kerose (xvii.), which is not easily obtained pure; and the analytical figure in our tabular statement (as we have indicated) is the mean of nine analyses of different specimens produced in a variety of ways.

The compounds present many points of interest; they distil, with at least partial decomposition, at singularly low temperatures, as we pointed out in our former paper. At low temperatures, too, they appear partially to decompose into fatty acid and hydrocarbon, thus:—

$$2(\text{ke}C_4H_4O_2) = \overset{\text{Kerose.}}{2\text{ke}} + \overset{\text{Acetic Acid.}}{\left.\begin{matrix} C_4H_4O_2 \\ C_4H_4O_2 \end{matrix}\right\}}$$

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* In this paper the atomic weight of carbon is written 6.

The explanation of the change is, that the small single molecules of acetic acid in combination with the kerose are very prone to combine with themselves to produce the double molecule of liquid or solid acetic acid.

Extending our enquiry to other members of the fatty acid family, we have observed that formic acid behaves quite differently from acetic acid. It appears to be quite incapable of forming these compounds.

Butyric acid and valerianic acid, on the other hand, form them quite readily.

Kerose xv. has given a compound with butyric acid yielding 53·10 per cent of the hydrocarbon. The theory for $C_{15}H_{15}C_8H_8O_2$ requires 54·40 per cent of $C_{15}H_{15}$.

Kerose xvii. has given the valerianic compound $C_{17}H_{17}C_{10}H_{10}O_2$, yielding 54·82 per cent of $C_{17}H_{17}$, the theory requiring 53·85.

Kerose xix. has given $C_{19}H_{19}C_{10}H_{10}O_2$, yielding 56·48, the theory requiring 56·60 of hydrocarbon.

The butyric compound was prepared like the acetic compounds, viz., by mixing the hydrocarbon with a moderate excess of the acid, and allowing the excess of acid to separate out as a lower layer of liquid.

The valerianic compounds were prepared somewhat differently. Valerianic acid was added to about its own volume, or rather more than its volume, of formic acid (with which it formed a perfectly homogeneous mixture), and then the hydrocarbon was poured in, considerably less than the theoretical quantity of hydrocarbon being employed. Under these circumstances the hydrocarbon seizes hold of its equivalent of valerianic acid, and forms the liquid valerianic compound, the formic acid playing the part of solvent medium. Here are the details of the experiment from the note-book:—

20 c.c. of valerianic acid mixed with 25 c.c. of formic acid, and then 20 c.c. of the kerose added. An upper layer of liquid, measuring 32 c.c., separated and washed with two small relays of formic acid, 2 c.c. and 3 c.c. respectively. Ultimate volume of the valerianic liquid, 31 c.c.

25·843 grms. taken for analysis and decomposed with weak ammonia, and the resulting hydrocarbon was washed and weighed. 14·695 grms. ∴ Oil = 56·48 per cent. Theory 56·60.

The valerianic compounds would seem to have more stability than the acetic compounds, inasmuch as they admit of being placed in contact with more than as much formic acid as valerianic acid *in the process of their formation.*

In the case of the acetic bodies only traces of formic acid are admissible in admixture with the excess of acetic acid. We are continuing the work.

Laboratory, New Malden, Surrey,
May 20, 1895.

ON GOLD SULPHIDE.

By A. DITTE.

The action of a current of hydrogen sulphide upon a dilute solution of gold chloride varies according to circumstances. If the liquid is neutral the first bubbles of the gas occasion a brown colouration, which deepens as the current passes, and when it is saturated it gives no deposit of a metallic sulphide. The solution is then deep brown, transparent, and passes through filters without losing any of its colour. I then left it to itself, in a closed vessel, at the ordinary temperature; it is slowly modified.

The gold sulphide is transformed in the course of twenty-four hours, or of a longer time; the liquid is still dark, but it is decolourised on filtration, or if left alone it slowly deposits gelatinous gold sulphide, which on agitation with water remains for a long time in suspension, forming a coloured liquid. The addition of a few drops of hydrochloric acid to the dark solution which passes through the filters, or to that which holds the gelatinous precipitate in suspension, rapidly causes the deposition of gold sulphide in the form of a black powder, and the liquid becomes colourless. This condition is reached at once if a currrent of hydrogen sulphide is passed into an acid solution of gold chloride.

Gold sulphide may thus take very different aspects from the soluble matter produced in a neutral solution, or obtained, as by Schneider, on dialysing a solution of gold cyanide in potassium cyanide saturated with hydrogen sulphide (*Berichte*, xxv., p, 2241) up to the dense black sulphide insoluble in water. This sulphide, if brought in contact with an alkaline sulphide, occasions various reactions.

If we gradually add sodium monosulphide to the black insoluble gold sulphide it gradually dissolves, and an excess of alkaline sulphide gives an orange-red solution having the odour peculiar to solutions of the alkaline persulphides.

This solution, if slowly evaporated in a vacuum, deposits aggregations of crystals formed by colourless transparent crystals radiating around a point. If well dried on porous porcelain their composition may be represented by the formula $Au_2S,2Na_2S,20H_2O$. These crystals blacken on the surface under the action of organic substances. They are very soluble in water, forming a colourless liquid in which dilute acids give at once a precipitate of gold sulphide.

If the alkaline sulphide is only in very slight excess we obtain an orange-yellow liquid, which in a vacuum deposits fine needles of the double sulphide,—

$$Au_2S,Na_2S,10H_2O,$$

and the mother-liquor on further concentration yields a supersaturated solution, which sometimes coagulates in a mass, and sometimes deposits small prisms, short, deliquescent, not containing gold, very soluble in water, yielding a yellow liquid in which dilute acids give an abundant deposit of sulphur. They consist of hydrated bisulphide, $Na_2S_2,8H_2O$.

Thus, on contact with sodium monosulphide in excess, gold sulphide passes into the state of aurous sulphide, Au_2S, which combines with the alkaline sulphide to form double sulphides, soluble in water without decomposition, whilst the sulphur set at liberty forms sodium bisulphide.

It is otherwise if the gold sulphide is in excess. A certain quantity dissolves, and then the undissolved portion decreases in volume, changes its colour, and after some days is converted into a dense, dull, greenish-yellow powder, formed of very minute crystals adhering together and opaque. This substance contains no sulphur; it is pure gold crystallised in the moist way. The small proportion of alkaline sulphide placed in contact with the excess of gold sulphide forms at first a double sulphide and sodium bisulphide. The latter continues to remove sulphur from the gold sulphide, setting the metal at liberty until the alkaline persulphide is saturated with sulphur. Lastly, the double sulphide in contact with excess of gold sulphide is decomposed and changed into alkaline persulphide depositing aurous sulphide. If, when all the alkaline sulphide is saturated with sulphur, there still remains gold sulphide undecomposed, it undergoes no further modification, the alkaline persulphide having no action upon it.

The gold sulphide, in fact, does not appreciably dissolve in a solution of sodium sulphide saturated with sulphur. On the other hand, a solution of gold sulphide in an excess of alkaline monosulphide, with the addition of fragments of sulphur, gives rise to the formation of a deposit of black sulphide, which increases in proportion as the sulphur dissolves, and when the liquid is saturated it contains merely traces of gold. Finally, the gold liberated does not give rise to any inverse reaction, for gold-leaf left for eighteen months in contact with a solution of sodium sulphide saturated with sulphur, at the ordinary temperature and in a sealed tube, is not affected by this liquid.

If for sodium sulphide we substitute that of potassium we observe analogous facts, but potassium sulphide—much more soluble in water than sodium sulphide—gives rise to double salts much more soluble in water than those formed with sodium, and more difficult to isolate in a state of purity. If we dissolve gold sulphide in a very slight excess of potassium sulphide we most frequently obtain a residue of metallic gold on operating in the cold, or at 30° to 40°. The filtered liquid, if evaporated in a vacuum, becomes a thick red syrup, ultimately depositing crystals. The crystals may be freed from their mother-liquor by depositing them upon a plate of very dry porcelain protected from moisture. The crystals are gold-coloured needles, very deliquescent, and very soluble in water, to which they give a yellow colour. If exposed to light they turn grey on the surface, and their composition may be represented by $Au_2S,4K_2S_2,12H_2O$. The mother-liquor coagulates into a mass on concentration *in vacuo*, whilst no definite compound is separated.

Potassium monosulphide in contact with an excess of gold sulphide deprives it of sulphur and separates metallic gold, exactly as takes place with sodium sulphide. The potassium sulphide saturated with sulphur has, like the sodium compound, no action in the cold, either upon gold sulphide or upon metallic gold. — *Comptes Rendus*, cxx., p. 320.

ON THE ADDITION OF ANILINE AND PHENYLHYDRAZIN TO BENZALMALONIC ESTER.

By R. BLANK.

Alkylidenmalonic esters have as yet been examined only slightly, and in a desultory manner, but in almost every investigation there was discovered a new remarkable additive reaction of the compounds of this type (general formula $R.CH:C(CO_2R_2)$).

Thus, Zalinsky observed that methylenmalonic ethylester is polymerised to a dimolecular compound, with a liberation of heat.

On saponifying this ester with potassa-lye he obtained the addition-compound of the corresponding acid with 1 mol. of water, whilst Tanator arrived, on using alcoholic potassa, at taradipimalic acid, the addition-product of the acid with 1 mol. of alcohol. A similar additive reaction was discovered by Claisen and Crismer on saponifying benzalmalonic ethyl ester with alcoholic potassa. On saponifying benzalmalonic methylester with methylic potassa there occurs an addition of water.

Ethylidenmalonic ester unites at a boiling heat with 1 mol. of malonic ester.

Finally, C. Liebermann demonstrated in an entire series of alkylidenmalonic esters the power of taking up additionally 1 mol. of sodium methyl (or ethyl) alcoholate.

I have now observed that the addition of aniline and phenylhydrazin to benzalmalonic ester takes place quite as smoothly.

Addition of Aniline to the Acid Benzalmalonic Methylester.

On adding 1 mol. aniline to the concentrated solution of the above acid ester in benzene there is formed, not the corresponding aniline salt, but an addition-compound of this salt with aniline, whence we may infer that the tendency of the ester-acid (or of its salt) to the addition of aniline is at least as great as its disposition to form a salt with the same base.

The subsidence of the compound begins soon after the ingredients have been brought into contact; it increases very slowly, and is quite considerable after two or three hours. A considerable part, however, remains in solution in which is retained the unconsumed part of the ester-acid. A further quantity of the compound may be precipitated by a further addition of aniline to the mother-liquor.

The new compound was washed with benzene, dried in a vacuum exsiccator over paraffin and sulphuric acid, and gave on analysis a composition corresponding to—

$$C_{23}H_{24}N_2O_4.$$

It has the form of white felted needles, melting at 97·5°; it is insoluble in water, but readily soluble in the ordinary organic solvents except ligroin. In dilute hydrochloric acid it forms at first a clear solution, which soon becomes turbid and gives off a smell of benzaldehyd. The same odour is perceptible if it is exposed to moist air.

According to analogy, with the additive reactions mentioned above, in which an easily mobile atom of hydrogen (or sodium) passes to the α-atom of carbon, whilst the residue attaches itself to the β-atom of carbon, we must regard the aniline addition-compound as an aniline salt of the β-anilidobenzylmalonic monomethyl ester, which is confirmed by the solubility of the compound in hydrochloric acid.

Addition of Aniline to the Neutral Benzalmalonic Methyl Ester.

β-Anilidobenzylmalonic methyl ester,—

$$C_6H_5.CH(NHC_6H_5).CH(CO_2CH_3)_2.$$

The ester is dissolved in a little benzene, and to the cold solution there is added 1 mol. of aniline. On the mixing, heat is liberated, and after standing at the common temperature for three or four hours the solution congeals to a white crystalline cake. The crystals are ground up and dissolved in a little benzene. If the cold solution is mixed with three vols. of ligroin, fine needles separate out, fusible at 117—118°.

For analysis the preparation was re-crystallised in the same manner and dried as above over paraffin and sulphuric acid in the vacuum exsiccator. Its composition is $C_{18}H_{19}NO_4$.

The same compound is formed by the reaction of two mols. aniline with one mol. of the ester. It is readily soluble in the ordinary organic solvents, except ligroin. In water it is insoluble. It dissolves in strong hydrochloric acid, but is precipitated unaltered on the addition of water.

The hydrochlorate is easily isolated; the anilidobenzylmalonic ester is dissolved in anhydrous ether, and a current of dry hydrochloric gas is passed into the solution.

In about half an hour the finely crystalline salt is filtered off, washed with ether, and dried in the exsiccator. The salt is very unstable, and loses hydrochloric acid on standing over soda-lime. On standing with water it is decomposed quantitatively into anilidobenzylmalonic ester and hydrochloric acid. After filtering off the ester, the hydrochloric acid in the filtrate may be determined as silver chloride. The composition of the salt is $C_{18}H_{19}NO_4.HCl$.

β-Phenylhydrazidobenzylmalonic methylester,—

$$C_6H_5.CH(NH.C_6H_5).CH(CO_2CH_3)_2.$$

This compound is formed under the same conditions as the aniline compound just described, which it resembles in its external aspect and in its relations of solubility. Its melting-point is at 94·5°. Its composition is $C_{18}H_{20}N_2O_4$.

If melted in a dry state, or if boiled in solution in absolute alcohol, it splits off malonic ester and is transformed into benzylidenhydrazon which melts at 157°, and on the addition of ferric chloride to its solution in concentrated sulphuric acid takes the well-known blue colour.

Benzylidenhydrazon has been recently obtained by Wislicenus on boiling benzalmalonic ester with phenylhydrazin in solution in absolute alcohol. The reaction may be conceived of as expulsion of malonic ester by phenylhydrazin.

The reaction occurs in two phases, the addition-compound obtained in the first phase being in the second split up into benzylenhydrazon and malonic ester.

Additive reactions between amines and non-saturated acids have been repeatedly observed, such as the addition of aniline to maleïc acid by Anschütz, and that of phenylhydrazin to maleïc and fumaric acids by P. Duden.—*Berichte*, xxviii., No. 2, 1895, p. 145.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 2nd, 1895.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Messrs. Vaughan Cornish, G. Cecil Jones, and Patrick H. Kirkaldy were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Morison, 7, O'Connell Street, Sydney, N.S.W.; Albert Joseph Simons, Elmhurst, New Barnet.

Of the following papers those marked * were read:—

*54. "*Studies on the Constitution of the Tri-derivatives of Naphthalene, No. 10. The Dichloro-α-Naphthols and Trichloronaphthalenes from 3 : 4-Dichlorophenyl-1-Isocrotonic Acid.*" By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

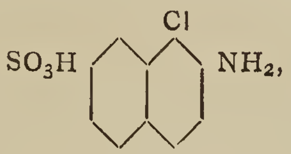
Having increased the number of known trichloronaphthalenes to 13 and determined their constitution (*cf. Proc. Chem. Soc.*, 1889, 48; 1890, 11, 84, 125 *et seq.*; 1891, 27; *B. A. Report*, 1891, 265), the authors naturally endeavoured to obtain the only remaining member of the series—the 1 : 2 : 1′ trichloronaphthalene; and failing to prepare this by any of the ordinary methods, they turned their attention in the autumn of 1890 to the two dichloronaphthols described by Erdmann and Schwechten (*Annalen*, cclx, 78; *cf.* cclxxv., 286), one of which was necessarily the 1 : 2 : 1′, and the other the 2 : 3 : 1′ derivative, as both were formed on distillieg 3 : 4-dichlorophenyl-1-isocrotonic acid. But as their discoverers had not ascertained the exact constitution of either, it was necessory to examine both; and through the courtesy of Dr. Erdmann the authors were enabled to undertake their investigation: they ultimately succeeded in preparing the desired trichloronaphthalene from the dichloronaphthol of lower melting-point. Special care was taken to purify the materials used (*cf.* Wynne, *Trans. C. S.*, 1892, 1053), as no other case was known of two isomeric chloronaphthols being simultaneously formed on condensing a chlorophenylisocrotonic acid. The purified dichlorophenylparaconic acid melting at 138°, obtained from 1700 grms. of 1 : 3 : 4-dichlorotoluene, weighed 326 grms.; on converting it into the isocrotonic acid and distilling this acid, the two isomeric dichloro-α-naphthols were obtained in the proportion of about one part of that of the lower to two parts of that of the higher melting-point.

1 : 2 : 1′-dichloro-α-naphthol crystallises from dilute alcohol in slender, flat needles, 2—3 m.m. long; it melts at 95° (not 83°, as stated by Erdmann and Schwechten). Its acetate crystallises in long, flat needles, melting at 87—88° (not 71—72°). On distillation with phosphorus pentachloride it yields a mixture of tri- with some tetrachloronaphthalene, separable by crystallisation from methylic alcohol. The trichloronaphthalene thus obtained crystallises in long, slender needles melting at 83°; its identity with the 1 : 2 : 1′-compound prepared by Clève's method has been established by a careful comparison, by optical methods, of the two products.

2 : 3 : 1′-dichloro-α-naphthol melts at 151°, and has all the properties ascribed to it by its discoverers; on distillation with phosphorus pentachloride it also yields a mixture of tri- and tetra-chloronaphthalene, from which the former can be separated by fractional crystallisation from methylic alcohol. The trichloronaphthalene crystallises in microscopic needles melting at 109°, and has been identified by optical methods with the 2 : 3 : 1′-derivative of this melting-point first described by the authors in 1890 (*Proc. Chem. Soc.*, 1890, 83).

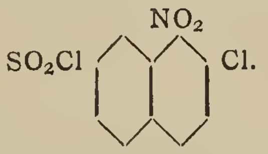
*55. "*Studies on the Constitution of the Tri-derivatives of Naphthalene, No. 11. The Trichloronaphthalene derivable from Clève's 1 : 2 : 2′-α-Nitrochloronaphthalenesulphonic Chloride.* By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

Of the three isomeric chloro-β-naphthylaminesulphonic acids described by the authors in their papers on the determination of the constitution of the heteronuclear di-derivatives of naphthalene (*Proc. Chem. Soc.*, 1889, 34 and 48), one (the so-called No. 3 acid) was shown to have the constitution—



and from this a dichloronaphthalenesulphonic chloride melting at 122—123°, and a trichloronaphthalene melting at 83—84°, were prepared, which presumably were also 1 : 2 : 2′-derivatives.

The important series of experiments on the nitration of the chloronaphthalenesulphonic chlorides carried out by Clève in 1892-93 includes the nitration of the 2 : 2′-derivative (*Ber.*, 1892, 2485; *Ofversigt*, &c., 1892, 417), from which he prepared a nitrochlorosulphonic chloride of the formula—



Although he obtained a dichloronaphthalenesulphonic chloride from this nitro-compound identical with that prepared by the authors from their No. 3 acid, yet by directly distilling the nitrosulphonic chloride with phosphorus pentachloride Clève obtained a product which he described as a trichloronaphthalene, which separated from alcohol in crystalline granules *melting at* 75·5°, and it was stated by him that this was identical with that prepared by Alén from α-nitronaphthalene-2 : 2′-disulphonic chloride (see further). And in describing his method of preparing 1 : 2 : 1′-trichloronaphthalene shortly afterwards (*Ofversigt*, 1893, 81), Clève regarded the substance he obtained as identical with that prepared by the authors from their No. 3 acid; he does not appear to have made any direct comparison of the products from the two sources, however.

Comparing these observations together, as in the following Table, it is evident that either a remarkable isomeric change occurs when a dichlorosulphonic chloride, but not when a nitrosulphonic chloride, is distilled with phosphorus pentachloride, or Clève's conclusions are erroneous.

	$Cl_2 \cdot SO_2Cl$.	$Cl_2 \cdot SO_2NH_2$.	Cl_3.
From No. 3 acid ..	122—123°	225—226°	83—84°*
From Clève's 1 : 2 : 2′ $NO_2 \cdot Cl \cdot SO_2Cl$ ..	124°	227°	75·5°†
From Clève's 1 : 2 : 1′ $NO_2 \cdot Cl \cdot SO_2Cl$ ..	138°	221° or 226°	83°*

A repetition of the author's work with the No. 3 acid on a large scale shows that, when pure, 1 : 2 : 2′-trichloronaphthalene has two melting-points, 88° and 84°. The higher melting-point is observed when the substance is first fused; but if it be allowed to solidify and then re-melted, the melting-point is found to be 84°, and usually does not vary from this until a crystal of the original substance is added to the fused mass between 60° and 80°.

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* From $Cl_2 \cdot SO_2Cl$ by distillation with PCl_5.

† From $NO_2 \cdot Cl \cdot SO_2Cl$ by distillation with PCl_5.

On repeating Clève's investigation of the 1 : 2 : 2'-nitrochloronaphthalenesulphonic chloride, it is found that not only does the trichloronaphthalene obtained from this substance—by converting it into the dichlorosulphonic chloride and distilling this with phosphorus pentachloride —melt at 88° and 84°, as above described, but that even Clève's own method—distillation of the nitro-derivative with phosphorus pentachloride—also leads to a like result: thus, on once crystallising from alcohol 39 grms. of the product prepared by the latter method, a first separation of no less than 28 grms. was obtained which had the double melting-point 88° and 84°, whilst, of the remainder, 5 grms. more were eventually obtained pure by fractional crystallisation, 3 grms. melting at 75—76°, and the remainder at intermediate temperatures.

In fine, the 1 : 2 : 2'-trichloronaphthalene prepared either by Clève's or the authors' method, melts at 88° or 84°, and not at 75·5°. That the two are identical is also shown by the fact that both yield similar derivatives, notably a monosulphonic acid affording a potassium salt, $C_{10}H_4Cl_3{\cdot}SO_3K+H_2O$, which crystallises in sparingly soluble flat needles, and a *chloride* which is sparingly soluble in benzene, and crystallises in small rhombs melting at 173°. That Clève is in error in regarding the trichloronaphthalene from the authors' No. 3 acid as the 1 : 2 : 1'-derivative is further shown by the fact that the monosulphonic acid prepared from this latter modification affords an anhydrous potassium salt crystallising in flat needles, and a *chloride* crystallising in prismatic needles melting at 105°.

*56. "*Studies on the Constitution of the Tri-derivatives of Naphthalene, No. 12. The Trichloronaphthalene derivable from Alén's α-Nitronaphthalene-2 : 2'-Disulphonic Chloride.*" By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

By nitrating 2 : 2'-naphthalenedisulphonic chloride, Alén obtained a nitro-derivative, from which, by distillation with phosphorus pentachloride, a componnd was formed which melted at 75·5°, and was regarded by him as a trichloronaphthalene (*Ofversigt*, 1884, 97). This compound, the [θ-]derivative, was regarded by the authors as impure 1 : 3 : 3'-trichloronaphthalene (*cf. B. A. Report*, 1891, 265), and not investigated until Clève announced its supposed identity with the product obtained from the 1 . 2 . 2'-α-nitrochloronaphthalenesulphonic chloride. A repetition of Alén's work has established the correctness of the authors' view as against that of Clève.

The 1 : 2 : 2'-α-chloro-β-naphthylaminesulphonic acid (No. 3 acid) can be converted into the *xanthate*—

$$EtO{\cdot}CS{\cdot}S{\cdot}C_{10}H_5Cl{\cdot}SO_3K+H_2O,$$

which crystallises in minute prisms, and this into the sparingly soluble *sulphide-sulphonate*,

$$[S{\cdot}C_{10}H_5Cl{\cdot}SO_3K]_2+\tfrac{1}{2}H_2O$$

—by Leuckart's method (*J. pr. Chem.*, [2], xli., 218—from which the 1 . 2 . 2'-α-chloronaphthalenedisulphonic acid is obtained by oxidation with permanganate solution (*cf. Proc. Chem. Soc.*, 1893, 166).

On hydrolysing the Alén nitrodisulphonic chloride melting at 138° with aqueous caustic potash, a *potassium* salt (containing $3H_2O$) is obtained, which by reduction with ferrous sulphate and caustic potash is converted into the very soluble salt of the amido-acid. The *acid potassium* salt ($+3H_2O$) crystallises in slender, readily soluble needles, and is convertible, by Sandmeyer's method, into an α-chloronaphthalenedisulphonic acid isomeric with that obtained from the No. 3 acid, as is evident from the Table.

	From No. 3 acid, by xanthate method.	From Alén's nitro-acid.
$Cl{\cdot}C_{10}H_5(SO_3K_2)$	$\frac{1}{3}H_2O$	$2H_2O$
$Cl{\cdot}C_{10}H_5(SO_2Cl)_2$	prisms, m.p. 144°	dimorphous— prisms, m.p. 114° needles, m.p. 127°
$C_{10}H_5Cl_3$	m.p. 88° and 84°	80·5°

When prepared by distilling the corresponding chlorodisulphonic chloride with phosphorus pentachloride, the trichloronaphthalene from the Alén acid melts at 80·5° after once crystallising it, and even when prepared by Alén's method, *i. e.*, by distilling the nitrodisulphonic chloride with phosphorus pentachloride, melts at a higher temperature than 75·5° after it has been once crystallised: thus, 9 grms. of product from this source gave on the first crystallisation 6 grms. melting at 78—79°, from which 5 grms. melting at 80·5° were eventually obtained, whilst of the residue some melted at 75—76°, and some as low as 65—68°. That the trichloronaphthalene melting at 80·5° obtained by either method is identical with the 1 : 3 : 3'-derivative of this melting-point (*Proc. Chem. Soc.*, 1890, 129; 1891, 27) is clearly shown by the behaviour on sulphonation, as they all yield a monosulphonic acid affording a monohydrated potassium salt crystallising in long, slender needles, and a *chloride* crystallising from benzene in radiate groups of long needles melting at 154°.

*57. "*Studies on the Constitution of the Tri-derivatives of Naphthalene.* No. 13. *The α-Naphthylamine-2 : 2'-disulphonic Acid of Freund's German Patent* 27346." By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

Through the kindness of Messrs. Casella and Co., the authors were furnished with a supply of the acid sodium salt of the α-naphthylamine-2 : 2'-disulphonic acid which had been isolated from the mixed product obtained by working under the conditions of Freund's German Patent 27346. The acid sodium salt,—

$$NH_2{\cdot}C_{10}H_5(SO_3H){\cdot}SO_3Na+3H_2O,$$

crystallises in tufts in long slender needles, easily soluble in hot water. By the hydrazine method it is converted into naphthalene-2 : 2'-disulphonic acid (characterised by conversion into the chloride crystallising from benzene in prisms melting at 157°, and into 2 : 2'-dichloronaphthalene melting at 114°). On treatment by the Sandmeyer process it gave a chlorodisulphonic acid, the *chloride*, $Cl{\cdot}C_{10}H_5(SO_2Cl)_2$, of which crystallised from a mixture of benzene and petroleum spirit in two forms, being dimorphous, namely, in clusters of small prisms melting at 114°, and in needles melting at 127°. After solidifying in the melting-point tube, the chloride melted constantly at 127°, although the lower melting-point, 114°, could again be obtained by adding to the fused substance at about 100° a crystal of this form. On distillation with phosphorus pentachloride, the chloride was converted into 1 : 3 : 3'-trichloronaphthalene melting at 80·5° which was characterised in the usual way by sulphonation. These results make it evident that the constitution of the acid is identical with that of the Alén acid just described, and that both are represented by the formula—

*58. "*The Non-existence of a Trichloronaphthalene Melting at 75·5°. The Formation of Chloro-derivatives from Sulphonic Chlorides.*" By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

From the foregoing it is evident that the "trichloronaphthalene" melting at 75·5°, described by Alén, was impure 1 : 3 : 3'-trichloronaphthalene, and that of Clève impure 1 : 2 : 2'-trichloronaphthalene. The impurity was in all probability tetrachloronaphthalene, as Clève's analysis (found 46·66 per cent Cl, against 45·98 per cent), and analyses of material of similar melting-point obtained by the authors by Clève's method (found 46·52 per cent Cl) and by Alén (found 46·48 per cent Cl), give numbers too high for a trichloronaphthalene. The quantity of material obtained from each of these two sources has been insufficient to admit of more than the pure trichloronaphthalene being isolated from the sulphonation product of each. The cause of the formation of tetrachloronaphthalene is probably to be sought in the fact that when phosphorus pentachloride is used to displace the NO_2 radicle in nitro-compounds, or the OH radicle in naphthol, its action is entirely different in character from that which is exercised in the case of sulphonic chlorides. In the case of the former, substitution occurs, and higher chlorination products are almost invariably formed; in that of the latter (*cf*, "B. A. Report," 1894, 268) the halogen derivative seems to be formed by the elimination of the SO_2 of the SO_2Cl radicle, not by a displacement of the radicle by chlorine derived from the pentachloride. The presence of the pentachloride seems to assist this elimination, and to increase the yield of product, but in most cases is not necessary for the action to pursue its course; and in certain instances it is advantageous that the chloride should be heated alone. Thus, when 1 : 1′-chloronaphthalenesulphonic chloride—which is known to be remarkable for the readiness with which it gives 1 : 4 : 1′-trichloronaphthalene on distillation with phosphorus pentachloride—is heated at a temperature rising from 200°—230° during three hours so long as SO_2 is evolved, a large quantity of 1 : 1′-dichloronaphthalene (m. p. 88°) is obtained, together with small quantities of α-monochloro- and a trichloronaphthalene; 1 . 2-α-chloronaphthalenesulphonic chloride is exceptional in affording a condensation product when heated without pentachloride, hydrogen chloride being constantly evolved, and only traces of 1 : 2-dichloronaphthalene being formed; but the other isomeric chloronaphthalenesulphonic chlorides behave, so far as examined, like the isomeric 2 : 4′-derivatives, thus—

	2 : 4′ $\beta Cl{\cdot}SO_2Cl$ with PCl_5.	2 : 4′ $\beta Cl{\cdot}SO_2Cl$ without PCl_5.	1 : 3′ $\alpha Cl{\cdot}SO_2Cl$ with PCl_5.	1 : 3′ $\alpha Cl{\cdot}SO_2Cl$. without PCl_5.
Temp. of action	190°	210—230°	195°	230—250°
Yield of 2 : 4′ Cl_2	92 p. c.	62 p. c.	65 p. c.	39 p. c.

The influence of the β- as compared with the α-position of the SO_2Cl radicle on the yield by both methods is evident from these data.

It may be pointed out that not only are all doubts as to the validity of the method of determining constitution by converting sulphonic chlorides into chloro-derivatives by distillation with phosphorus pentachloride set at rest by the agreement of the results obtained with and without pentachloride, but that independent and most important confirmation of the correctness of the conclusions arrived at is afforded by the fact that the same ultimate product is obtained by directly displacing NH_2 in an amido-compound by chlorine by the Sandmeyer-Griess method and indirectly displacing it by chlorine by first preparing the xanthate, then oxidising to sulphonic acid, and distilling the chloride of this acid alone or with pentachloride. Moreover, the general agreement of the authors' results is such that they believe they are justified in regarding their conclusions as final.

*59. "*Studies on the Constitution of the Tri-derivatives of Naphthalene.* No. 14. *The Fourteen Isomeric Trichloronaphthalenes.*" By Henry E. Armstrong, F.R.S., and W. P. Wynne, D.Sc.

The thirteen isomeric trichloronaphthalenes considered in connection with methods leading to the elucidation of their constitution in the authors' previous papers (*cf. Proc. Chem. Soc.*, 1889—1890), have not as yet been tabulated by them with their melting-points, it being deemed desirable to set all doubts at rest before doing this. Since 1890 they have entirely revised their earlier work and extended it in order to obtain the various trichloronaphthalenes in quantities of from 35 to 50 grms.; additional methods of preparation have also been devised with the object of accumulating evidence from as many sources as possible capable of throwing light on the relative positions of any pair of radicles in the tri-derivatives. As a result, the trichloronaphthalenes have not only been characterised by conversion into monosulphonic acids, but their constitution has been determined by so many methods that there is now no room for doubt that the fourteen predicted by theory are known, and that they have the melting-points assigned to them in the accompanying table. The number of methods of preparation, each involving the determination of the relative positions of at least one pair of radicles, is given in brackets in the last column. Details regarding the properties of the trichloronaphthalenes, especially of their sulphonic derivatives, are reserved for the complete publication, as these have no bearing on the general questions considered in these notes. (See Table below).

*60. "*The Solubilities of Gases in Water under varying Pressure.*" By E. P. Perman, D.Sc.

The method used may be briefly described as follows:—A rapid current of air is aspirated through a saturated solution of the gas, the solubility of which is to be determined, and the amounts of the gas drawn off in given intervals of time, as well as the amount left in solution at the end of the experiment, are estimated, usually by a volumetric method. A curve is then drawn by plotting the amounts of gas (in grms.) in solution against the time (in minutes) during which the aspiration has been carried on. A series of tangents to this curve are then drawn; their values give the *rates* at which the gas is drawn off at different concentrations, and these *rates* are measures of the pressure of the gas in solution. The rates were then plotted against the corresponding concentrations. If the rate is proportional to the concentration, the pressure of

Trichloronaphthalenes.

State of knowledge at the end of 1888.				Constitution and melting-points assigned by				
				Armstrong and Wynne, 1889-90.		Clève, 1892-93.	Armstrong and Wynne, 1895.	
[α-]	1 : 2 : 3.	M. p.	81° (Widman)	1 : 2 : 3	81°	—	81°	[2] *
	1 : 2 : 4.	,,	92° (Clève)	1 : 2 : 4	92°	—	92°	[1]
			—	1 : 2 : 4′ (1 : 2 : 5)	78·5°	77° ; 76	78·5°	[5]
	? : 2 : 6.	,,	91° (Forsling)	1 : 2 : 3′ (1 : 2 : 6)	92·5°	90°	92·5°	[4]
			—	1 : 2 : 2′ (1 : 2 : 7)	83—84°	75·5°	88° and 84°	[3]
			—	1 : 2 : 1′ (1 : 2 : 8)	—	83°	83·5°	[2]
[γ-]	1 : 3 : ?.	,,	103° (Widman)	1 : 3 : 4′ (1 : 3 : 5)	103°	103°	103°	[5]
[θ-]	α : 2 : 7.	,,	75·5° (Alén)	1 : 3 : 3′ (1 : 3 : 6)	80·5°	—	80·5°	[6]
[η-]	α : 2 : 6.	,,	113° (Alén)	1 : 3 : 2′ (1 : 3 : 7)	113°	—	113°	[7]
[β-]	1 : ? : ?	,,	90° (Atterberg)	1 : 3 : 1′ (1 : 3 : 8)	87° and 90°	—	89·5° and 85°	[2]
[δ-]	1 : 4 : 5.	,,	131° (Atterberg)	1 : 4 : 4′ (1 : 4 : 5)	131°	130°	131°	[4]
[ε-]	2 : ? : ?	,,	65° (Clève)	1 : 4 : 3′ (1 : 4 : 6)	66° and 56°	65° and 56°	66° and 56°	[6]
[ζ-]	2 : ? : β	,,	56° (Widman)					
			—	2 : 3 : 4′ (2 : 3 : 5)	109·5°	—	109°	[2]
			—	2 : 3 : 3′ (2 : 3 : 6)	91°	—	91°	[4]

* Number of methods, each involving a determination of the relative positions of at least one pair of radicles, by which the compound has been prepared.

the gas is also proportional to the concentration, and the law of Henry holds good for the gas in question.

The aspiration was carried on in a series of five wash-bottles; the first to contain water, which makes up for loss by evaporation of the solution in the second; the second to contain the solution of the gas; the other three to contain water or some solution to absorb the gas drawn off. Air was drawn through the series of flasks by means of a water air-pump, and a regulator was placed between the pump and the flasks.

Experiments were made with solutions of ammonia, chlorine, bromine, carbon dioxide, hydrochloric acid gas, sulphuretted hydrogen, and sulphur dioxide. Henry's law was found to hold good for chlorine, bromine, carbon dioxide, and sulphuretted hydrogen, while ammonia, hydrochloric acid gas, and sulphur dioxide showed large deviations which appear to be caused by the formation of compounds of these gases with water.

Discussion.

In reply to questions from the President and Professor Armstrong as to whether the air drawn through the solution of the gas becomes saturated, Dr. Perman stated that the air does not take up as much gas as it would if the current were extremely slow, and is therefore probably not saturated in this sense. He considered, however, that this fact does not invalidate the method. The amount of gas taken up by the air in a small interval of time will be proportional to the pressure of the gas in solution, just as the amount of aqueous vapour given up by a pan of water placed in a steady current of air would be proportional to the vapour-pressure of the water. The only necessary assumption is that the gases are "perfect," as they may certainly be taken to be for the purposes of the experiment.

*61. *The Existence of Hydrates and of Double-compounds in Solution.*" Part I. By E. P. Perman, D.Sc.

The effect upon the pressure of ammonia gas in an aqueous solution produced by dissolving various salts in the gaseous solution was investigated by the method described in the preceding paper.

The gas-pressure was unaltered by dissolving 3·9 grms. sodium chloride in 50 c.c. of ammonia solution containing 4·43 grms. of ammonia.

The pressure was also unaltered when 11·23 grms. of sodium sulphate, $Na_2SO_4 \cdot 10H_2O$, were dissolved in 50 c.c. of the ammonia solution; but on dissolving 3·8 grms. of the anhydrous sulphate in the same quantity of solution, the gas pressure was increased considerably, and the increase of pressure corresponded exactly to the increase of concentration which would be caused by a loss of 4·8 grms. of water, *i.e.*, $10H_2O$ for every next drop of sodium sulphate. The author regards this as conclusive evidence that the sodium sulphate exists in solution as a definite hydrate, $Na_2SO_4 \cdot 10H_2O$.

Silver chloride at once reduced the pressure of the ammonia when introduced into the solution, thus showing that some compound of silver chloride and ammonia was formed.

In a solution containing 4 grms. of ammonia, and saturated with silver chloride, the pressure was the same as in an ammonia solution containing 2·8 grms. of ammonia in the same bulk (50 c.c.); 1·2 grms. had therefore entered into combination with the silver chloride, 0·0235 grm.-molecules (from Bodländer's table of solubilities of silver chloride in ammonia solution). This corresponds to a compound $AgCl \cdot 3NH_3$. The existence of the same compound is also indicated in more dilute solutions.

62. "*Derivatives of π-Bromocamphoric Acid.*" By F. Stanley Kipping, Ph.D., D.Sc.

The syrupy acid obtained on treating π-bromocamphoric acid with alcoholic potash (*Proc. C. S.*, 1895, 148, 33) has now been obtained in a crystalline condition, and further analysis has confirmed the view that it is a hydroxycamphoric acid of the composition $C_{10}H_{16}O_5$. (Found C = 55·1, H = 7·4; theory, C = 55·5, H = 7·4 per cent).

When π-bromocamphoric acid is warmed with aqueous potash it is first converted into an acid which is very readily soluble in water, and which is probably the hydroxy-acid just mentioned; on continued treatment, however, this initial product is transformed into a more soluble well-defined acid of the composition $C_{10}H_{14}O_4$. (Found C = 60·4, H = 7·1; theory C = 60·6, H = 7·1 per cent). This compound separates from water and dilute alcohol in large fern-like forms which seem to contain water of crystallisation, but it is deposited from a mixture of chloroform and benzene in transparent anhydrous crystals melting at about 165°; apparently it is a saturated compound as its solution in sodium carbonate does not decolourise potassium permanganate at ordinary temperatures.

An isomeride of this acid is formed in small quantities, together with other products, when π-bromocamphoric acid is heated with quinoline under suitable conditions. (Found C = 60·5, H = 7·1; theory C = 60·6, H = 7·1 per cent); this compound crystallises from water and dilute alcohol, in which it is rather sparingly soluble, in beautiful stellate forms and in six-sided plates, and melts at about 226°; it sublimes unchanged, does not give an anhydride when warmed for some time with acetic chloride, and its solution in sodium carbonate does not decolourise potassium permanganate even on boiling for a short time; these properties seem to show that it is a saturated lactonic acid.

The acid melting at about 165° is readily oxidised by warm very dilute nitric acid, the final product being a crystalline acid, which seems to have the composition $C_{10}H_{14}O_6$. (Found C = 52·0, H = 6·1; theory C = 52·2, H = 6·1 per cent); this substance is very readily soluble in water from which it is deposited in six-sided plates which seem to contain water of crystallisation; it crystallises from ethereal chloroform in lustrous prisms, melting at about 195°. When heated with acetic chloride for a short time, this acid is converted into a substance which crystallises in beautiful six-sided prisms, melting at about 250°; this product dissolves in sodium carbonate with effervescence and is probably an anhydride acid of the composition $C_{10}H_{12}O_5$, but an analysis has not yet been made.

The results indicated above afford additional facts on which to base a constitutional formula for camphoric acid, but their theoretical import cannot be discussed here.

63. "*Paraheptyltoluene and its Derivatives.*" By F. Stanley Kipping, Ph.D., D.Sc., and O. F. Russell.

This paper contains an account of *p*-heptyltoluene, $C_6H_{13} \cdot CO \cdot C_6H_4Me$, and of various other compounds which have been referred to in previous notes (Kipping, *Proc. Chem. Soc.*, 1893-94, 128, 208; and 136, 60.

64. "*Note on the Formation of a Phosphate of Platinum.*" By Robert E. Barnett.

On subliming commercial phosphorus pentoxide over red-hot spongy platinum in a current of oxygen, part of the platinum is converted into a yellow substance, which being insoluble in aqua regia can thus be separated from the excess of the metal.

The analysis agrees with the formula PtP_2O_7. It is a greenish yellow powder of rel. dens. 4·856, and is stable at a red heat unless reducing gases are present. It is insoluble in water, acids, and aqueous alkalis, but is decomposed by fusion with potassium sodium carbonate. Aqueous hydrogen sulphide slowly decomposes the compound; the exact nature of the products is still being investigated.

Saturated Ammonium Orthophosphate.—K. Kraut.—P. Schottländer is not the first chemist who has analysed this salt. Its composition is—Ammonia 25·22, phosphoric acid 34·97, and water 39·91.—*Zeit. Anorg. Chemie*, vii., Part 6.

NOTICES OF BOOKS.

Stephens's Catechism of Practical Agriculture. New Edition, Revised and largely Re-written, by James Macdonald, F.R.S.E., Secretary of the Highland and Agricultural Society; Editor of the Fourth Edition of "The Book of the Farm," &c. Twenty-second Thousand. Edinburgh and London: W. Blackwood and Sons. 1895. Crown 8vo., pp. 85.

We do not greatly admire the catechetical form of instruction in any subject; but, reserving this point, we must own that Mr. Macdonald has produced a compact and intelligible manual.

Perhaps a few subjects might have been advantageously mentioned which the author has overlooked. Thus, as regards hay and grain, the use of the Gillwell drying-machine might have been recommended for weeping summers and autumns. The inventor has been honoured with the gold medal of the Highland and Agricultural Society. Something might have been said concerning the growth of hops, of apples and pears for cider and perry, and of small fruits for the manufacture of jams, which have now an increasing commercial importance. Several other crops might have been mentioned, which, although they do not afford scope for the investment of millions of capital and the employment of thousands of labourers, should, on the good old principle of "many a mickle makes a muckle," not be overlooked.

CORRESPONDENCE.

FLIES AND MICROBES.

To the Editor of the Chemical News.

Sir,—In your notice of the last Conversazione of the Royal Society you refer to an exhibit purposing to show that flies may be carriers of microbes, and you state that it "proves the reality of the transmission of infection, *i.e.*, of pathogenic microbia, by flies." It perhaps should be pointed out that this is no new discovery, it having been already proved in various ways by several investigators, who, moreover, actually employed pathogenic bacteria in their experiments. Thus, Celli fed flies with the sputum of phthisical patients, and also with pure cultivations of typhoid, anthrax, and other bacilli, and was able to subsequently demonstrate the presence of these organisms in the excreta of these flies. Sawtschenko points out the possibility of cholera bacilli multiplying within the bodies of flies, he having found enormous numbers of these bacilli in the alimentary tract of flies after a lapse of seventy two hours from their first infection, although subsequent to that they were fed only with sterile broth, with the object, if possible, of washing out the bacilli. Moreover, Cattani and Tizzoni placed minute quantities of cholera bacilli on the bodies of flies, and found that after keeping them for an hour and a half and longer, when introduced into sterile culture media these flies gave rise to typical growths.

It may be of interest to the exhibitor, and possibly save him unnecessary trouble, if he will refer back to *Nature* of March 23, 1893, where he will find an article on flies and disease germs.—I am, &c.,

X. Y. Z.

TEST FOR MORPHINE IN UREA.

To the Editor of the Chemical News.

Sir,—In your "Notes and Queries" in the Chemical News (vol. lxxi., p. 246), I noticed that A. R. P. enquires for the best source of obtaining information as to the most delicate tests for morphine in urea.

I suppose by this he means that he has a mixture of morphine and urea. I should suggest his trying the following tests:—

1. By the ammonium sulpho-selenite test, prepared by dissolving 1 part of ammonium sulpho-selenite in 20 parts of concentrated sulphuric acid, which I expect will give him a greenish blue, changing through violet to red colour.

2. Add a little acetic acid until just acid, neutralise, and add neutral Fe_2Cl_6, the morphine blue colour is formed; if Fe_2Cl_6 is in excess, a green tint is observed; on warming the blue colour disappears and a blood-red is produced, showing the presence of an acetate. In very dilute solution Fe_2Cl_6 fixes no colouration, but is reduced to ferrous salt, and the solution will give Turnbull's blue; on the subsequent addition of potassium ferricyanide 1 part of morphine in 100 parts of water can be detected.

Perhaps it would be advisable to do some blank experiments with the above tests, and he might also look up some German translations on organic analysis at some of the scientific libraries, such as the Patent Office and the Chemical Society library.—I am, &c.,

P. L. Aslanoglou.

VOLUMETRIC DETERMINATION OF SUGAR BY AMMONIO-CUPRIC SOLUTION.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lxxi., p. 235) appears a paper by M. Zdenek Peske, in which the ordinary Pavy method is modified by using a layer of "pure paraffin oil" to exclude the air during the operation.

I am happy to bear testimony to the efficacy and convenience of this proposal, and am the better able to do so that I happen to be the originator of it. I described exactly the same method at a meeting of the Society of Public Analysts held in June, 1894; and details of the process were published in *The Analyst* for August, 1894, p. 181, *The Lancet* for July 28, 1894, p. 213, and the *Pharmaceutical Journal* for the same date, p. 90.

M. Peske's paper was read in abstract before the Chemical Society on March 21, 1895, by Professor Brauner, with whom, I believe, M. Peske had been working. Immediately the first accounts of it appeared, I informed the Secretaries of the Society that I had anticipated M. Peske, and received in return a promise that the fact should be communicated to Professor Brauner. Evidently postal communication on the Continent is very slow and uncertain, but English work is assiduously read and English ideas appropriated. The natural supposition would be that M. Peske had hit on the same idea, independently, but subsequently to me, were it not that in the abstract of his paper published in No. 150 of the *Proceedings of the Chemical Society* he makes reference to my "rather lengthy modification" of Fehling's method. As this can only refer to a modification of Fehling's test which was published in the journals above quoted as part of the same communication which suggested the use of mineral oil for excluding the air during Pavy titrations, it is difficult to resist the conclusion that M. Peske was aware of my prior employment of the plan. I am far from thin-skinned in such matters, but the present annexation is one which I cannot allow to pass without protest.—I am, &c.,

Alfred H. Allen.

67, Surrey Street, Sheffield,
May 18, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 18, May 6, 1895.

Researches on the Earths of Cerite.—P. Schützenberger.—Will be inserted in full.

Action of Fluorine upon Argon.—Henri Moissan.—Will be inserted in full.

On Fluted Spectra.—Arthur Schuster.—This does not admit of useful abridgment.

Researches on Mercurous Sulphate, Nitrate, and Acetate.—Raoul Varet.—Thermo-chemical determinations not suitable for abstraction and not of sufficient importance for insertion in full.

Presence of Chitine in the Cellular Tissue of Mushrooms.—Eugene Gilson.—The author has obtained pure chitine from *Agaricus campestris*, and has also shown its presence in ten other species of mushroom. (This, we may add, is another proximate principle common to the animal and the vegetable kingdoms).

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. ix., No. 112.

On a MS. of Gonperille entitled "The Art of Dyeing Cotton."—Jules Garçon.—The disinterment of a MS. work by F. D. Gonperille, published in 1807. In this bulky work the author made known the use of *chayaver*, a plant with which the dyers of India produced reds.

Programme of Prizes to be Awarded.—In 1896 the grand gold medal will be awarded for the greatest improvement in the mechanical arts; in 1897 for the greatest advance in the chemical arts; in 1899 in agriculture.

The Argenteuil prize of 12,000 francs will be awarded in 1898 for the invention most useful in perfecting French industry.

The Society's great prize of 12,000 francs will be awarded in 1895 for the discovery most useful to French industry.

The Henri Giffard prize of 6000 francs will be awarded in 1896 for signal services to French industry.

The prize of 1000 francs for workmen in manufactories of chemical products is awarded yearly.

The Melson's prize of 500 francs will be awarded in 1896, for an application of physics or chemistry to electricity, ballistics, or hygiene.

A prize of 1000 francs will be awarded in 1896 for the utilisation of a waste product.

A prize of 2000 francs will be awarded in 1896 for a new process for the production of fuming sulphuric acid or sulphuric anhydride.

A prize of 2000 francs will be awarded in 1896 for a new improvement in the production of chlorine.

A prize of 1000 francs will be awarded in 1896 for a new alloy useful in the arts.

A prize of 1000 francs will be awarded in 1896 for a substitute for sulphuric acid in dyeing, especially on silks.

A prize of 2000 francs will be awarded in 1896 for the discovery of procedures capable of yielding useful organic products.

MEETINGS FOR THE WEEK.

Monday, 27th.—Society of Arts, 8. (Cantor Lectures). "Japanese Art Industries," by Ernest Hart, D.C.L.
Tuesday, 28th.—Royal Institution, 3. "Thirty Years' Progress in Biological Science," by Prof. E. Ray Lankester, F.R.S.
— Society of Arts, 8. "The Decoration of St. Paul's," by Prof. W. B. Richmond, A.R.A.
— Medical and Chirurgical, 8.30.
— Institute of Civil Engineers, 8. (Anniversary).
— Photographic, 8.
Wednesday, 29th.—British Astronomical Association, 5.
Thursday, 30th.—Royal, 4 30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Instruments and Methods of Spectroscopic Astronomy," by William Huggins, D.C.L., F.R.S.
Friday, 31st.—Royal Institution, 9. "The Radiant Heat from the Moon during the Progress of an Eclipse," by The Earl of Rosse.
Saturday, June 1st.—Royal Institution, 3. "Elizabethan Literature," by Prof. Edward Dowden, D.C.L.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1853.

ON ARGON AND HELIUM.*

I have examined the gas which is found enclosed in meteoric iron. The meteorite which I used was from Augusta County, Virginia, U.S.A., and had been examined by Prof. Mallet. The analysis has been published in the *American Journal of Science*, July, 1871; it contains—

Fe	88·4
Ni	10·2
Co	0·4
P	0·3
C	0·2

besides traces of Cu, Sn, Mn, Cl, S, and SiO_2. We have obtained 45 c.c. of a gas, some per cents of which disappeared on detonation with oxygen. The residue being submitted to electric sparks in presence of caustic soda underwent a slight contraction. The residue was dried with caustic soda, and I found, by means of the spectroscope, that it consists of argon, of which it shows all the characteristic marks.

We may also observe the yellow line of helium, and on comparing it with a sample of pure helium, the identity was certain. It does not coincide with the D lines of sodium.

It is interesting to find the presence of argon in a substance foreign to the earth, though it has not been recognised in the sun.

It must be remarked in conclusion that there are no lines except those of argon and helium.

I am still occupied with helium; its density is 3·88, and the ratio of the specific heats is 1·66, as with argon.

It is remarkable that the difference between the densities of argon and helium is 16, which is the case for the members of the first group and those of the second.

Helium is found in most of the minerals of the rare earths which I have examined. It is very curious that it has not been recognised earlier.—*Comptes Rendus*, cxx., p. 1049, May 13, 1895.

ON ARGON.

By HERMANN SCHILD.

Berthelot and Mendeleeff in the endeavour to locate argon in the periodic system have each given the opinion that argon is a tri-atomic modification of nitrogen, just as ozone is a modification of oxygen.

As I am not in the position to institute experiments which might promote the decision of this question, I should be happy if the following remarks could be taken into consideration in the further investigation on the nature of argon. I refer here to a treatise ("Stahl und Eisen," 1888, No. 1) which I have published in concert with Prof. B. Kirsch.

The several theorems in that essay touching on the allotropic modifications of the elements have the following contents:—An allotropic modification of an element cannot, as such, enter into a chemical combination, but can only form a molecular allocation, because, in a chemical compound, an element only comes into view as an atom and an allotropic modification exists only as a polyatomic molecule. If an element exists in the form of a modification it must, on entering into a chemical combination, be resolved into atoms and be only then combined. What can be perceived from the formulæ given by Schönbein—the first who assumed the chemical combination of a modification of an element—cannot be brought into harmony with the understanding that the modification of elements to a molecule arise by the combination of atoms of one and the same elements in different numbers.

After this reference I must remind the reader that Ramsay has liberated argon from clèveite by means of sulphuric acid, and that Berthelot has succeeded in bringing argon into chemical combination with benzene; lastly, azoimide (N_3H) is known.

If argon is triatomic nitrogen, it is only in molecular apposition and not in chemical combination, since chemically combined nitrogen has not hitherto been liberated as argon, but, on the contrary, the nitrogen obtained chemically has always, in opposition to atmospheric nitrogen, proved free from argon. Further, in the elementary analysis of Berthelot's compound of argon and benzene or its decomposition-products (if, as it can scarcely be supposed, we are not concerned with a mere molecular apposition) the argon would be set free as nitrogen, just as we cannot obtain argon from N_3H. The elementary analysis of Berthelot's compound leads us to anticipate the most weighty revelations. The production of argon from nitrogen still requires verification.

Passing to another subject, I venture to remark that the memoir above mentioned is mainly engaged with the existence of iron carbide. As it has lately been found practicable to produce the carbides of various metals, it would be a boon to science if, by producing iron carbide by Moissan's method, a contribution could be furnished to decisions on iron and steel according to their percentage of carbon.—*Chemiker Zeitung*, 1895, No. 37.

THERMOMETRIC ANALYSIS.

We are indebted to the courtesy of Mr. J. Barker Smith, L.R.C.P., for notes of his "Thermometric Method for the Estimation of Urea." He writes:—

In some articles on rheumatism published in *Medical Reprints*, 1890, July, August, and September, I showed how urea could be easily estimated in urine by placing 1 c.c. of urine in a pipette with 5 c.c. of a *good sample* of solution of chlorinated soda of the present Pharmacopœia, and, after the reaction, noting the quantity of the mixture expelled. In solving the fallacy of temperature I have discovered a still simpler method of estimating urea in urine, a method which is also applicable to the albumenoids of foods. My method is completed if necessary in the short space of three minutes, and is especially useful for the bedside in fever cases, also in the wards of the hospital, and as a control test in the physiological laboratory.

The general practitioner will find the test the simplest and most rapid of any of the tests for the quantitative estimation of urea. An ordinary cylindrical phial is found and fitted with a soft cork, a long half-ounce phial answers admirably. Measure 5 c.c. of water into the phial, and file a mark on the phial at the level of 5 c.c., add another c.c. of water and file another mark immediately over the first. No further measure is required. We pour solution of chlorinated soda up to the first mark, and then place the stem of a small thermometer into the phial, and after one minute note the temperature, *e.g.*, 56° F.; we then remove the thermometer and pour in urine to the second mark (1 c.c.), replace the cork, and holding the phial by the rim we shake vigorously for ten *seconds*, remove the cork and replace the thermometer; after about thirty *seconds* the temperature is read off which is in ratio to the urea. Suppose the temperature after the reaction is 64° F., then the difference between

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* Extract of a letter from Prof. Ramsay to M. Berthelot.

the first and second temperature is *eight* degrees, and this number multiplied by the factor 0·2 gives the percentage of urea, in this case 1·6 per cent (8 × 0·2). Of course, each bottle can be tested with a definite solution of urea by those who do not accept the data of a 2 per cent solution giving 10° of heat.

A suitable thermometer is brought out by Messrs. Maw, Son, and Thompson, called my "Biological Thermometer," similar to a clinical thermometer, with an extended scale and without an indicator. However, I have just found that a small foreign thermometer, with inside index, is sent out by Dollond, Ludgate Hill, for the small sum of eighteenpence, and I find it answers very well for urea estimations by my new method.

The author further states that we may estimate albumenoids in solution exactly in the same manner as we estimate urea, *i.e.*, with a good specimen of solution of chloride of soda (sodium hypochlorite) as described in the *Provincial Medical Journal* for November.

The factor to multiply the degrees of heat by, to obtain the percentage of albumenoids, is just three times greater than that used in the estimation of urea. The factor for urea is 0·2, and the factor for albumenoids is 0·6; the process is the same as for urea. 5 c.c. of the chlorinated soda solution are placed in the half-ounce phial, 1 c.c. of milk, &c., as for the estimation of urea.

Suppose the milk gives 6° of heat, as indicated by my "Biological Thermometer," then we say it contains 3·6 per cent of albumenoids (6 × 0·6). We shall not be able to estimate very weak solutions of albumens, not much weaker than ½ per cent; at the same time we can see that traces of albumen in urine do not affect the estimation of urea.

Suppose we have a substance like flour or bread. Weigh 1 grm. of bread and put it into a small mortar; add 4 c.c. of water and rub it into a paste; now add 3 or 4 c.c. of liquor potassæ, and rub into a jelly; add water to 10 or 20 c.c.; finally, estimate as for urea—*e.g.*, *percentages*.

Examples.	Biol. therm. percentage.	Actual percentage.
Serum albumen	0·9	0·88
Peptone	3·15	3·2
Fibrine	0·9	0·8
Gluten	0·72	0·78
"	1·35	1·33

The values in the second column are found by oxidimetry (*vide* "Milk," p. 8; or *Invention*, from October, 1893, to July, 1894).

Dr. Barker Smith, in a communication to the *Provincial Medical Journal*, extends this thermometric method to the estimation of alcohol in spirituous liquor. He mixes a known volume of water with an equal volume of the spirit in question, both at the same temperature. He ascertained the temperature before and immediately after mixing, when the heat read off is a measure of the percentage of alcohol.

If, *e.g.*, 5 c.c. of water mixed with 5 c.c. of spirit give 10½° of heat, the spirit is a rectified or methylated spirit. If the heat is 7½° we conclude that the spirit or tincture is of proof strength. Dr. Barker Smith admits that "we shall not be able to value the alcoholic mixtures accurately, not much nearer perhaps than 5 per cent of alcohol by measure." The author proposes extending his method to the estimation of uric acid and the urates.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on May 6th, Sir James Crichton-Browne presiding. The following were elected Members:—Mr. Henry Irving, Mr. Henry Perigal, Mrs. Slingsby Tanner, Mr. Ernest H. Fry, Mr. Thomas Muir, Mr. Harold Smith, and Mr. W. S. Smith. The special thanks of the Members were returned to Mr. George Matthey for his donation of £50 to the fund for the promotion of experimental research at low temperatures.

RESEARCHES ON THE EARTH OF CERITE

By P. SCHUTZENBERGER.

In a previous communication upon cerium I had the honour of calling the attention of the Academy to the differences presented by the successive and fractionated crystallisations of cerium sulphate obtained by the method of Debray, concerning the weight of oxide, (CeO_2), which remains as a residue on igniting these sulphates to redness.

The first and most abundant crystallisations, purified by several re-crystallisations, always re-dissolving the first deposits, yield a product the composition of which is constant.

From this sulphate—which, for the sake of convenience, we will designate as sulphate of Ce No. 1, or of Ce_I—we obtain the following results, according to the manner of analysis:—

1. Ignition to cherry redness, considering the residue as binoxide.
   Atomic weight .. .. .. $Ce_I = 139·5$
2. Ignition of the sulphate to white redness, considering the residue as binoxide.
   Atomic weight .. .. .. $Ce_I = 139·0$
   138·8
3. Determination of the sulphuric acid by barium chloride, the determination being made with the precautions indicated in my former memoir.
   Atomic weight .. .. .. $Ce_I = 139·5$ grms.
4. Synthesis of the sulphate, taking as the point of departure the pure binoxide of a canary-yellow colour, in a state of very fine division, obtained by burning the oxalate in the air at various temperatures.
   Dull redness .. .. $Ce_I = 142—143$
   Cherry redness .. .. $Ce_I = 139·7$
   White redness .. .. $Ce_I = 139$ to 138·8

If, on the contrary, we take the crystals of sulphate obtained from the last mother-liquors on precipitation with alcohol, washing in alcohol, drying and dehydration, re-solution and re-crystallisation, the results are clearly distinct, and seem to show the presence of alien earths.

In order to elucidate this question I have made a thorough study of the methods of determining the atomic weight of cerium founded on the analysis or the synthesis of the sulphate.

As an instance we have the analysis of a sulphate from these last mother-liquors, which I shall provisionally name cerium sulphate No 2, or Ce_2.

In appearance it exactly resembles cerium sulphate No. 1.

We had previously applied all the operations capable of removing the yttrium bases, the alkalies, the alkaline earths, didymium, and lanthanum.

This sulphate forms with potassium sulphate a double salt, totally insoluble in a saturated solution of potassium sulphate; the mother-liquor of the double sulphate does not show any trace of earthy oxides.

1. Analysis by determining the sulphuric acid by means of barium chloride.
   Atomic weight deduced .. $Ce_2 = 138·75$
2. Crystallisation water of the sulphate deposited at 75° in the form of colourless prisms, isomorphous with cerium sulphate No. 1.
   Per cent .. .. 13·66
3. Analysis of the anhydrous sulphate (dried at 44° in a bath of the vapour of sulphur) by calcination to bright redness, almost white.
   a. Anhydrous sulphate used .. .. .. 2·120
   Oxide obtained of a decided rose-colour 1·272
   Atomic weight calculated, on supposing the oxide to be binoxide .. .. .. $Ce_2 = 136·0$

b. Anhydrous sulphate used .. .. .. 1·8593
Reddish oxide obtained.. .. .. .. 1·1180
Atomic weight found, calculating the oxide as binoxide .. .. Ce_2 = 135·7

4. Synthesis of the sulphate by means of a finely-divided oxide, of a yellowish-rose colour, obtained on burning the oxide in air at dull redness.
Oxide used .. .. 1·1756
Anhydrous sulphate obtained.. 1·9262
Oxide not acted on deducted .. 0·6055

Atomic weight on calculating the oxide as binoxide—

Ce_2 = 142·5.

The comparison of these results with those of cerium sulphate No. 1 shows that—

1. The atomic weight of Ce_1, deduced from the determination of the sulphuric acid, is greater by about 1 unit than that of Ce_2 obtained in the same manner.
   Ce_1 = 139·45. Ce_2 = 138·75.
2. The atomic weights of Ce_1 and Ce_2, determined by synthesis of the sulphates from oxides obtained on igniting the oxalates at dull redness in contact with air, differ but little.
   Ce_1 = 143·3, Ce_2 = 142·5,
   and are both higher than the atomic weights obtained by determining SO_4.
3. The atomic weights deduced on igniting the sulphates at a bright red, almost white heat, calculating the residues as binoxides, are very distinct.
   Ce_1 = 139. Ce_2 = 136 to 135·7.

For cerium No. 1 this last method gives a result very close upon the typical analysis founded on the determination of SO_4 by Cl_2Ba. The cerium binoxide from Ce_1 only undergoes a very slight loss of oxygen at white redness. On the contrary, for Ce_2 the discrepancy is considerable, for we have 138·75 on the one hand and 135·7 on the other.

Hence the bioxide of Ce_2, the existence of which is established by the results furnished by the synthesis of the sulphate from the oxide of the oxalate, undergoes, by ignition at bright redness bordering upon whiteness, a sensible loss of oxygen, and is partially reduced to the state of a sesquioxide.

4. The residue from the ignition of the two sulphates at white redness present very different colours; for Ce_1 it is nearly white, and for Ce_2 it is a light rosy-brown.
5. The sulphates of Ce_1 and of Ce_2 are isomorphous, and contain the same quantity of water of crystallisation.

It is infinitely probable that the sulphate Ce_2 analysed above is merely a mixture of the ordinary cerium sulphate No. 1 with some other sulphate.

The residual oxide from the ignition at whiteness of the sulphate Ce_2 might have as its formula $(Ce_2O_4)_2Ce_2O_3$, taking for Ce the value 138·75 deduced from the determination of the sulphuric acid. The following facts corroborate this view:—

Hitherto we have operated only on the crystals deposited in heat (75°) during the evaporation of the crude sulphates obtained by the classical treatment of cerite (see the former memoir).

The quantity of product obtained in this manner is very slight, and does not allow of the fractionation being carried further.

The treatment of the last mother-liquors has enabled me to arrive at a product which we may call Ce_3.

The analysis of the sulphate, after a prolonged purification, has given the following results:—

1. By the synthesis of the sulphate from the oxide yielded on igniting the oxalate at dull redness, the oxide being taken as binoxide,—
   Ce_3 = 142·4.
2. By determining the sulphuric acid with $BaCl_2$,—
   Ce_3 = 137·1.
3. By igniting the sulphate at a redness bordering upon whiteness,—
   Ce_3 = 128 to 130.

These last results lead me to ascribe to this oxide, which is of a brownish-red, the formula—

$$(Ce_{\frac{2}{3}}O_4).(Ce_{\frac{2}{5}}O_3), \text{ or } C_{\frac{4}{3}}O_7.$$

This oxide when ignited is attacked by concentrated sulphuric acid only with great difficulty. To convert it into sulphate, the sulphates formed must be several times re-ignited after solution in water.

Hitherto I have not found it practicable to resolve the sulphate of Ce_3 into products of a distinct composition by fractionated crystallisations. It may be that we are here in the presence of a definite product.

It is still also possible that the sulphate of Ce_3 represents a double sulphate of Ce_1, yielding on ignition $Ce_{\frac{2}{1}}O_4$, and another sulphate of Ce giving on ignition $Ce_{\frac{2}{4}}O_3$. On this hypothesis we may calculate approximately the atomic weight of Ce_4. It would be equal to 134.

$$\frac{134+140}{2} = 137.$$

However this may be, these experiments show that cerium oxide is in cerite accompanied by small quantities of another earth of lower atomic weight, 137 or 134, capable, like cerium oxide (Ce_2O_3), of conversion into a binoxide, the sulphate of which, isomorphous with that of cerium, forms, like the latter with the alkaline sulphates, insoluble double sulphates, and the binoxide of which after ignition presents a reddish-brown colour, even without the intervention of didymium.—*Comptes Rendus*, cxx., p. 962.

ON THE COMPOSITION OF CERTAIN SOILS OF SOUTH INDIA.

By CECIL MASSEY.

As the systematic investigation of soils of various parts of the world can hardly be over-estimated, it is a pleasure for me to give the composition of a number of soils from Coorg, South India. The samples for each analysis were prepared by the most careful methods, being thoroughly mixed, and finally made to pass through a sieve of 30 meshes to the linear inch. The following results were obtained from these soils, which were collected from four different fields of arable land:—

	No. I.	No. II.	No. III.	No. IV.
Moisture	6·676	6·216	7·020	7·423
*Organic matter and combined water	3·701	4·303	3 968	4·835
Ferric oxide	4·204	3·821	4·999	3·320
Alumina	5·395	6·222	6·186	6·831
Lime	0·863	0·993	0·824	0·999
Magnesia	0·210	0·300	0·255	0·352
Potash (K_2O)	0·623	0·734	0·582	0·682
Soda (Na_2O)	0·375	0·335	0·300	0·410
Phosphoric acid (P_2O_5)	0·396	0·569	0·713	0·812
Sulphuric acid (SO_3) ..	0·120	0·207	0·186	0·200
Carbonic acid (CO_2) ..	0·211	0·302	0·190	0·235
Chlorine	0·024	0·030	0·094	0·076
Silica and insol. matter	77·202	75·968	74·683	73·825
	100·000	100·000	100·000	100·000
* Nitrogen, per cent..	0·691	0·832	0·79	0·857
Specific gravity ..	2·503	2·56	2·46	2·392

As these soils came from India it was thought advisable to examine them for microbes. It may be mentioned, *en* *passant*, that the soil of all cultivated land is teeming with microbes, whose principal function is to aid in supplying plants with their necessary food. But the exact nature of the work performed by the majority of soil microbes is still unknown. The four Indian soils (after several weeks' desiccation in transit) gave the following numbers of microbes:—

No. I.	196,000	per grm. of soil.
No. II...	253,000	,, ,,
No. III.	210,000	,, ,,
No. IV.	264,000	,, ,,

No new species were found in the samples. The nitrous and nitric microbes of Frankland, Warington, and Winogradsky were present.

In conclusion, it may be stated that the fields from which the samples were taken are for the growth of coffee.

ON A NEW METHOD FOR THE SEPARATION OF COPPER AND CADMIUM IN QUALITATIVE ANALYSIS.

By **ALLERTON S. CUSHMAN.**

The successful separation of small quantities of cadmium from copper has been one of the difficult operations of qualitative analysis. The method depending upon the solubility of copper sulphide in potassium cyanide is not considered by most chemists so desirable as the method of boiling the mixed sulphides in dilute sulphuric acid, on account both of its inferior delicacy and of the unpleasant character of the reagent. The last edition of Crookes's "Select Methods in Chemical Analysis" has to say on this subject:—"Cadmium sulphide dissolves with the greatest facility in boiling dilute sulphuric acid, which has no action on copper sulphide. On precipitating, by sulphuretted hydrogen, a solution containing not more than 1 m.grm. of cadmium mixed with 1000 m.grms. of copper, and boiling the black precipitate for a few seconds with dilute sulphuric acid (1 part concentrated acid and 5 parts of water), a colourless filtrate is obtained in which an aqueous solution of sulphuretted hydrogen produces an unmistakeable precipitate of yellow cadmium sulphide. Another solution of the same composition was mixed with an excess of potassium cyanide and treated with sulphuretted hydrogen gas. A distinct yellow colouration was observed; a deposit likewise took place, but so slowly that in delicacy the former experiment appears to have a considerable advantage, especially since a solution of *pure* copper in potassium cyanide also gives rise to a yellow colouration when submitted to the action of sulphuretted hydrogen."

Undoubtedly the sulphuric-acid separation is an exceedingly delicate one, when performed under the conditions detailed in the foregoing. When, however, the amount of copper present is large, and the filtration of the mixed sulphides is prolonged, traces of copper are almost certain to find their way by oxidation into the sulphuric acid solution, in which case, on addition of hydrogen sulphide, the yellow colour of the cadmium sulphide is invariably masked by the brown tinge of the sulphide of copper. Very small quantities of cadmium dissolved in an excess of dilute sulphuric acid may very easily escape detection on further dilution and addition of hydrogen sulphide, unless extreme care, cleanliness, and rapidity in filtration have been observed. Certainly few metals oftener escape detection in elementary practice than does cadmium when present in small quantity with copper.

In the solutions that were given out for analysis to the students in this laboratory, it was noticed that when cadmium and antimony were present in the same solution the cadmium frequently failed to be precipitated by hydrogen sulphide out of acid solution, but made its appearance with the precipitates of Groups III.—IV. It seemed that the only explanation of this lay in the fact that a strong solution of sodium chloride had been added to each mixture in which antimony was put, in order to prevent the separation of basic compounds of the latter metal. In the course of an investigation bearing upon this subject, it was found that when cadmium sulphide was treated with a saturated solution of one of the alkaline chlorides in the presence of dilute hydrochloric acid, it immediately dissolved to a clear solution with evolution of hydrogen sulphide. As far as can be learned, this reaction between cadmium sulphide and solutions of the alkaline chlorides in the presence of dilute hydrochloric acid has been nowhere noted. The ability of the alkaline chlorides to form double salts with many of the metals is well known, and, according to V. Hauer, cadmium chloride unites with the alkaline chlorides, and chlorides of the alkaline earths, to form compounds of the general formulæ:—$4RCl,CdCl_2$; $2RClCdCl_2$; $RClCdCl_2$ (*Pharm. Centralb.*, 1858, 292, 787; 1856, 766). On boiling cadmium oxide and cadmium carbonate with ammonium chloride solution a double crystalline compound has been obtained with the formula $2NH_4Cl,2CdCl_2,H_2O$ (Graham Otto, "Aufl." 5, iii., 828).

In order to see if a strong neutral solution of ammonium chloride had any action on cadmium sulphide, the following experiment was made:—A solution of cadmium nitrate was precipitated by hydrogen sulphide, and the precipitate thoroughly washed by decantation with boiling water until free from last traces of sulphuretted hydrogen. The precipitate was then thrown on a filter, sucked dry, and finally dried at 100°. A quantity of this dried calcium sulphide was suspended in a concentrated solution of ammonium chloride in a flask which was connected with a Varrentrapp-Will tube containing a solution of lead acetate. The temperature of the mixture was then gradually raised without producing any precipitate in the bulb-tube until protracted boiling had taken place, when a decided precipitate of lead sulphide appeared in the tube. It is a well-known fact that solutions of ammonium chloride become acid on prolonged boiling owing to dissociation and escape of ammonia (*Ann. Chem.*, Liebig, cxxviii., 189; Graham Otto, iii., 485). As the partial reaction in this case only began after prolonged boiling, it is probable that it was due to the formation of free hydrochloric acid in the solution. On addition of dilute hydrochloric acid to the mixture in the flask, the cadmium sulphide immediately dissolved. On repeating the foregoing experiment, using sodium chloride instead of ammonium chloride, no hydrogen sulphide was given off except in the presence of free hydrochloric acid. In a general way the reaction is perhaps best expressed by the following:—$CdS+2RCl+2HCl=CdCl_2,2RCl+H_2S$.

This solubility of cadmium sulphide in acidified concentrated solutions of the alkaline chlorides renders possible an exceedingly delicate method of testing for cadmium. If to 2 c.c. of a solution containing a small amount of cadmium, 10 c.c. of a saturated solution of salt and a few drops of dilute hydrochloric acid be added, hydrogen sulphide fails to produce any precipitation even up to saturation of the liquid by the gas. If now a few drops of dilute ammonia be allowed to flow down the side of the tube a distinct yellow ring or layer of cadmium sulphide appears at the junction of the two liquids. By this method 1 c.c. of a solution containing 0·1 m.grm. of cadmium sulphate developed a distinct yellow ring in a few minutes, while 3 drops of the same solution, equal to an amount less than 0·01 m.grm. of cadmium, developed a perceptible ring on standing half an hour.

The fact that copper sulphide has been found quite insoluble in the reagents offers an easy and delicate method of separating the two metals. When the metals are present in comparatively large quantity it is only necessary to treat the mixed sulphides with an excess of a strong solution of salt and a little dilute hydrochloric acid, when, on warming, the cadmium sulphide entirely dissolves. On dilution of the filtrate and addition of hydrogen sulphide, the cadmium sulphide is re-precipitated. The method is more accurately carried out in this laboratory as follows:—About 2 c.c. of the solution containing the two metals is made slightly acid with hydrochloric acid, and about 20 c.c. of a saturated salt solution added, the solution warmed, and hydrogen sulphide passed through until the copper is all precipitated and the hydrogen sulphide is present in excess. The copper sulphide is then filtered off through a dry filter, and the filtrate run into a dry test-tube. The filtrate collected in the tube should be perfectly clear, as the slightest dilution begins to precipitate the cadmium. Therefore if a few drops of water be allowed to run down the side of the test-tube, a yellow line will be formed at the junction of the two liquids if cadmium is present. Diluted ammonia may be substituted for water with advantage if the amount of cadmium present is very small, as it developes the yellow layer more rapidly than water does. On the other hand, if traces of other metals are present through incomplete removal in the group separations, the result will be obscured by the use of ammonia.

This method has been thoroughly tested with mixtures of solutions of copper and cadmium in varying proportions, and has been found extremely sensitive. Sometimes it has been found that, when very minute quantities of copper are present, the copper sulphide is precipitated in the strong solution of sodium chloride in so finely divided a condition that it is impossible to remove it completely by filtration. In this case the addition of a few drops of a solution of copper sulphate and re-precipitation with hydrogen sulphide obviates the difficulty.

In the hands of students the method has given uniformly good results when carried out with the ordinary care necessary to the success of all analytical processes. As some other metallic sulphides, notably those of lead and bismuth, are found to be soluble in strong acidified solutions of the alkaline chlorides, these metals must be as completely removed as in any other test for cadmium.

The bearing of these reactions with lead, bismuth, and cadmium sulphides, on qualitative and quantitative separations, will be more fully studied in this laboratory in the future. The simplicity of the reagents used, and the delicacy of the test for cadmium, will probably commend the method to chemists and instructors in qualitative analysis.—*American Chemical Journal*, vol. xvii., No. 5.

ON THE ATOMIC WEIGHT OF OXYGEN.

SYNTHESIS OF WEIGHED QUANTITIES OF WATER FROM WEIGHED QUANTITIES OF HYDROGEN AND OXYGEN.

By EDWARD W. MORLEY.

Many most valuable contributions to our knowledge of the atomic weight of oxygen have been made within ten years by Rayleigh, by Dittmar and Henderson, and by Scott, in England, by Leduc in France, by Thomsen in Denmark, and by Cooke and Richards, by Keiser, and by Noyes in America. My own experiments began many years before I learned that others were at work on the subject; but as no assistance could be afforded me, and as, till after the completion of the experiments described in this paper, the whole expense fell upon me, the progress made was so slow that it often seemed hardly worth while to go on.

The process used by Berzelius and Dulong, and by Dumas was first studied. Perhaps the opinion unfavourable to its precision which was formed may be modified by the experience of others, but until our knowledge of the properties of cupric oxide becomes such that we can easily prepare an oxide free from everything but copper and oxygen, the process can hardly be made capable of satisfactory precision. But it cost a year to come to this decision.

It also cost much time to learn how, with ease and certainty, to prepare hydrogen of sufficient purity. When this was accomplished, the method of weighing the gas directly had to be chosen. Some of my globes had a capacity of 21·5 litres, so that 1·8 grms. of hydrogen could be weighed in one of them. Since the weight of such a globe can be determined with a mean error of less than a tenth of a m.grm. in a single weighing, the process is not an unpromising one. But while it is easy to prepare pure hydrogen, and easy to weigh it, it is by no means easy to introduce it into the globe without contamination, either by mercurial vapour, from a mercurial air-pump, or by organic vapours from the lubricant of a piston air-pump. The difficulties could be surmounted, if no alternative method were available. But there is a better method, and it is easy.

One method of directly weighing hydrogen is, to weigh a suitable gas-bottle with its drying train, then to generate hydrogen in it by the solution of a metal in an acid or in an alkali, and then weigh again. Some of the forms of apparatus which were tried would permit me to weigh over 4 grms. of hydrogen in each experiment. But it was impossible to procure easily a metal which gave pure hydrogen, or hydrogen which could be purified with a simple purifying train. Nothing would answer my purpose except zinc re-distilled in a vacuum so as to free it from carbon.

There remained only the costly recourse to the method depending on the use of palladium. Chirikoff seems first to have suggested the use of palladium as a means of purifying hydrogen. I began experimenting with the present investigation in mind in 1883, though on a small scale.

The experiments to be described in this paper consist of twelve syntheses of weighed quantities of water from weighed quantities of hydrogen and of oxygen. The hydrogen was absorbed in 600 grms. of palladium; the oxygen was weighed in two globes, in the form of gas. Full details of the experiments are ready for a publication of the Smithsonian Institution, to which those are referred who care to know the nature of the apparatus used, and to see the quantities determined by the balance or the eudiometer, unmodified by any computation. The present paper is but a brief abstract of one part of that paper, giving the final results of each of the experiments, and such a general description of the apparatus as may be sufficient for many.

Apparatus for Producing and Weighing Water.

The apparatus for producing and weighing water consisted of a thin glass tube some 22 c.m. long and 25 m.m. in diameter (Fig. 1). Midway in its length were inserted two tubes, ending within in two platinum jets parallel to the axis of the tube. Just above these jets were two platinum wires for inflaming the jet of hydrogen or of oxygen. The gases came to the jets through drying tubes filled with phosphorus pentoxide, so that the uncombined gases could enter, but the water produced could not escape, if the apparatus were properly used. The ends of the drying tubes were furnished with ground joints by which they could be joined to the apparatus for regulating the admission of the gases. The volume of the apparatus was not far from 250 c.c., and the weight nearly 100 grms. Before using it, it was exhausted to the ten-thousandth of an atmosphere, and closed by fusion. Its volume was determined and it was then weighed accurately against a counterpoise of the same volume and of 35 or 40 grms. greater weight.

Apparatus for Weighing Hydrogen.

My plant for weighing hydrogen contained 600 grms. of palladium; in the first and second experiments this was divided between two tubes, but in the rest it was all in one tube. Some trifling modifications of its form were made after each accident to it; all these are mentioned in the paper to be issued by the Smithsonian Institution. In the final form no stopcock was used on this tube; but even in those experiments in which the stop-cock was still attached to the tube, it was never used for any purpose except to regulate the current of gas for a moment. A most fruitful source of annoyance, or even of serious error, was avoided by depending solely on fusion for closing this tube. The tube containing palladium having been connected by fusion to the source of hydrogen shown at Fig. 1 in my paper on the "Volumetric Composition of Water" (*Am. Journ. Sci.*, xli., 225), the palladium was heated, and a current of the gas was passed for half an hour or more. The tube was then closed by fusion, the metal was cooled, and the gas was passed into it to saturation. The tube was then again opened and a current of the gas was passed for two or three hours, so as to remove any nitrogen which might conceivably have accumulated, after which it was closed by fusion at all points, its volume was determined by hydrostatic weighing, and its weight was determined by the method of reversal, using a counterpoise of the same volume and the same weight. The observations of weight were repeated at intervals.

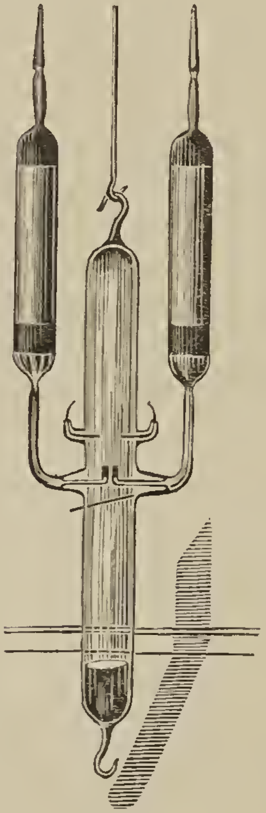

FIG. 1.

Apparatus for Weighing Oxygen.

The two globes used for weighing oxygen contained 20·0 and 21·5 litres. They were provided with counterpoises which were equal to them in volume when the globes were exhausted, and the expansion of the globes produced by filling them with gas was compensated, the compensation being a simple and accurate method of dispensing with the observations of pressure and temperature which would have been necessary in order to compute corrections for differences of volume. The globes were exhausted with a Toepler pump to one part in thirty or fifty thousand, and filled with pure and dry oxygen. They were weighed as stated before. It was thought that the amount of mercury vapour which contaminated the oxygen was negligible, experiments seeming to justify this opinion. That the oxygen was free from chlorine, although made from potassium chlorate, was proved by suitable examination of the water produced from it.

Balance.

The balance used was made by Becker, of Rotterdam, and carries a kilogrm. in each pan. It was procured for this investigation, and has been used for nothing else. It was set up in a room of nearly constant temperature, on the stone cover of a closet or cave of a little more than a metre in each internal dimension. Under the balance, fastened to the under side of this stone cover, is a reversal apparatus by means of which any one of three pairs of objects may be suspended from either pan of the balance without opening the cave or approaching the balance. With this apparatus, objects to be weighed were placed in the cave, each pair in its desiccator, and left in dry air for hours before weighing. After weighing each pair of objects at least four times, by reversal, at intervals of at least half an hour, it was hoped that the weights might be considered fairly determined. The probable errors of the results seem to justify this hope.

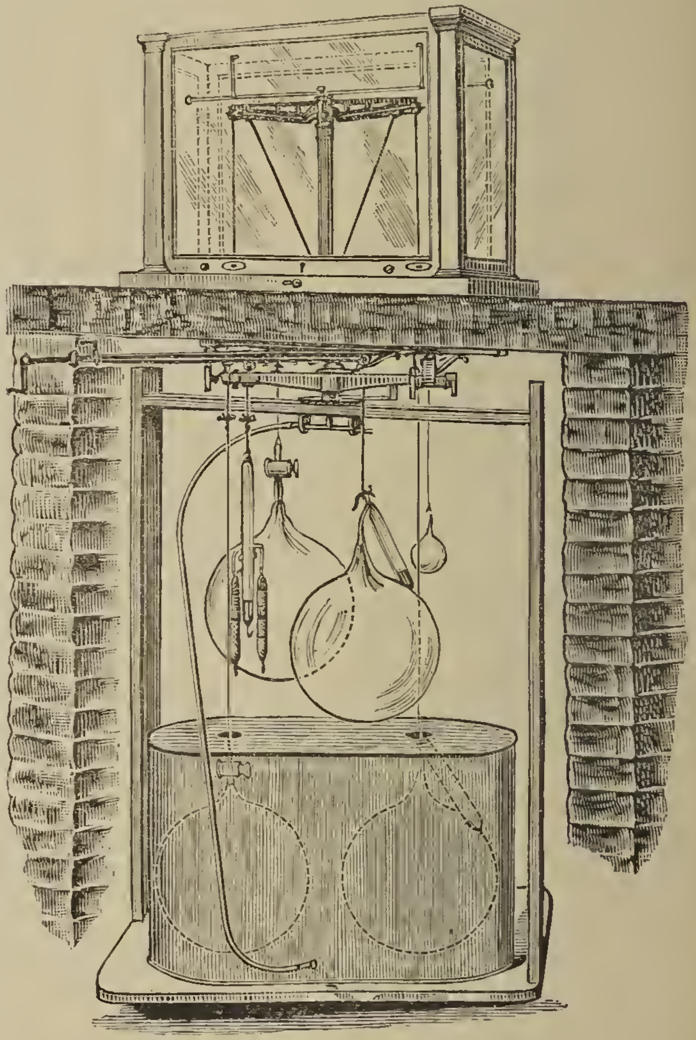

FIG. 2.

Fig. 2 shows the balance and the mechanism for weighing by reversal. The apparatus was photographed while supported temporarily for the purpose, and the drawing made from the photograph as accurately as the artist could well do it, but some details are not quite correct. Hooks attached to the pans of the balance pass down through the stone cover of the vault. Six hooks carrying the globes and other objects are supported by six arms just below the stone. By means of the handles seen well to the left, any one of these six hooks can be engaged in either of the first pair, and then left attached to it, and free from contact with the arm. The current of dry air needed to supply the desiccators was introduced through the axis of the reversal mechanism, as suggested by the rubber tube in the drawing. The desiccators for the second and third pairs of objects are not shown.

Combining the Gases to Produce Water.

When the hydrogen, the oxygen, and the apparatus for containing the water produced, had been weighed, the apparatus was set together. The apparatus for producing water was opened by breaking off the tubes near the ground-joints of the drying tubes; of course, taking means to prevent the admission of moisture with the entering air. The apparatus was then connected to the system of stopcocks and gauges for controlling the admission of the gases. To this same system were then connected the palladium tube and the two globes of oxygen. Before these were opened to admit gases to the system, the combustion apparatus and the system of tubes were exhausted by a Toepler pump which was permanently connected to the apparatus. After the pump was shut off, the gases were admitted to the connecting tubes and into the combustion apparatus itself, where they were ignited by sparks between the wires for the purpose. Immersion in water kept this part of the apparatus at a suitable temperature.

After the combustion was ended, the palladium tube and the globes for oxygen were closed, and the water which had been produced was cooled to −20°, so as to make the tension of its vapour small. The Toepler pump again exhausted the apparatus, and the gas withdrawn from the globes and the tube of palladium, but remaining unconsumed in the apparatus, was transferred to an eudiometer. The combustion apparatus was closed by fusion and weighed together with the parts removed in the manipulation of opening and closing it. The same was done with the tube containing palladium, which was also weighed hydrostatically, to detect any change of volume due to heating. When the globes had been weighed, it was known how much had been withdrawn from each source of gas. The unconsumed residue being measured and analysed, and the proper subtraction being made, it was known how much of each gas had been combined to form water, which gave the ratio sought. From the weight of water produced, compared with the weight of hydrogen used, was obtained a second determination of the ratio.

No rubber joints were used about the apparatus; all connections were made by fusion, except where parts had to have their weight preserved unchanged, when they were connected to adjoining pieces by suitable ground-joints made tight with paraffin.

The results of the twelve experiments made by this method are given in the following table.

Weights of hydrogen, of oxygen, and of water formed, with ratios deduced:—

Hydrogen.	Oxygen.	Ratio.	Water.	Ratio.
3·2645	25·9176	15·878	29·1788	17·877
3·2559	25·8531	15·881	29·1052	17·878
3·8193	30·3210	15·878	34·1389	17·873
3·8450	30·5294	15·880	Apparatus broken.	
3·8382	30·4700	15·877	34·3151	17·881
3·8523	30·5818	15·877	34·4327	17·876
3·8297	30·4013	15·877	34·2284	17·875
3·8286	30·3966	15·878	34·2261	17·879
3·8225	30·3497	15·879	34·1742	17·881
3·8220	30·3479	15·881	34·1743	17·883
3·7637	29·8865	15·881	33·6540	17·883
3·8211	30·3429	15·882	34·1559	17·878
Means ..		15·8792±0·00032	17·8785±0·00066	

Besides the full details of experiments here briefly described, the paper in the hands of the Secretary of the Smithsonian Institution contains three series of determinations of the density of oxygen under normal conditions at the sea-level in latitude 45°; two series of similar determinations for hydrogen by the processes hitherto used, which are rejected for a suspected source of error incident to such determinations; three series of determinations of the density of hydrogen by a new method which avoids the error suspected, which were carried out with two independent apparatus; and a determination of the volumetric composition of water by a process which is, in one respect, similar to that lately used by Leduc. The combination of these quantities gives a third determination of the atomic weight of oxygen, of which the trustworthiness, as far as can be judged from probable errors, is equal to that of any determination hitherto made; and it agrees absurdly well with the two results from the syntheses. In this work on the densities I have had generous help from Mrs. Amasa Stone, from Messrs. Warner and Swasey, from Mr. C. W. Wason, from the East Cleveland Railroad Company, and the succeeding corporation, the Cleveland Electric Railway Company, and from the Smithsonian Institution; which I am glad of the opportunity to acknowledge.

The following table gives the more important results of the work on the densities and volumetric composition, together with the final results of the experiments described in the present paper. To it is appended a table showing the results of previous experimenters, which Professor F. W. Clarke had revised for a forthcoming work, and which he kindly furnished to me:—

Density of oxygen, latitude 45° ..	1·42895±0·000034
Density of hydrogen	0·08987±0·0000027
Ratio of densities	15·90c2 ±0·00061
Volumetric composition of water at 0°	2·0027 ±0·00014
Atomic ratio from densities and volumetric ratio	15·879 ±0·0011*
Atomic ratio, syntheses	15·8792 ±0·00032
Molecular weight of water, syntheses	17·8785 ±0·00066

Results of other Experimenters.

	Atomic ratio.
Berzelius and Dulong	15·894 ±0·057
Dumas	15·961 ±0·007
Erdmann and Marchand	15·975 ±0·011
Cooke and Richards	15·869 ±0·0020
Keiser, 1888	15·951 ±0 0011
Rayleigh, syntheses	15·89 ±0·009
Noyes..	15·897 ±0·0017
Dittmar and Henderson..	15·867 ±0·0046
Leduc..	15·881 ±0·013
Morley	15·879 ±0·0003

	Ratio of densities.
Regnault, corrected by Crafts ..	15·9105±0·0044
Rayleigh, 1888..	15·884 ±0·0048
,, 1892..	15·882 ±0·0023
Cooke..	15·890 ±0·0067
Leduc..	15·905 ±0·015
Morley	15·900 ±0·0006

Volumetric Composition of Water.

Scott	2·00285
Morley, eudiometer (reduced to 0°)	2·0008
Leduc	2·0038
,, corrected according to my reduction	2·0024

While the value 2·0002, which I obtained by direct measurement, is the value which I am certain would be obtained by others working with pure gases in an apparatus of the nature and dimensions used, it is obvious that the result is not a measurement of the quantity desired, but that it is complicated with a phenomenon which is hinted at by the fact that both my own experiments and those of Scott in an apparatus of similar dimensions, yield a result in which the volume of the oxygen comes out too large. But whether I shall have the means of elucidating the supposed cause remains for the future. I think we may safely trust the values obtained by Scott and by myself in our last determinations:—

Scott	2·00285
Morley	2·00270

—*American Chemical Journal*, xvii., No. 4.

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* Atomic ratio, from densities and volumetric ratio by Scott's experiments, 15·878.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, May 24th, 1895.

Captain W. de W. Abney, President, in the Chair.

Dr. Kuenen read a paper entitled "*On the Condensation and the Critical Phenomena of Mixtures of Ethane and Nitrous Oxide.*"

If the vapour of a pure substance is compressed at constant temperature, when a certain pressure is reached the vapour commences to condense and the pressure remains constant until all the vapour is liquefied. On taking the pressure and temperature as co-ordinates, and plotting the corresponding temperatures and pressures at which liquefaction takes place, a curve is obtained which is called the vapour-pressure curve, and this curve ends at the critical temperature and pressure of the given substance. On the other hand, if a mixture of two vapours is compressed at constant temperature, the pressure no longer remains constant while condensation is taking place, but gradually rises. The points at which condensation commences and ends lie on a U-shaped curve, having its vortex turned towards the direction of increasing temperature. Such a curve the author calls a "border-curve." The point at which a line parallel to the axis of p touches a border-curve corresponds to the critical point (R) of the given mixture. In all temperatures higher than that corresponding to R there is no condensation into liquid possible, while for any temperature below the critical temperature there are two vapour-pressures, one corresponding to the commencement and the other to the conclusion of liquefaction. The envelope of all the border-curves for mixtures containing different proportions of the two bodies is a curve, called the plaitpoint-curve, joining the critical points of the two constituents. The point of contact (P) of a border-curve with the plaitpoint-curve corresponds to the plaitpoint on van der Waal's thermodynamic surface. If when we go along the border-curve, starting from its lower branch, we first reach R, then P, and if we indicate the temperatures corresponding to P and R by T_P and T_R, then for temperatures between T_P and T_R, as the pressure is increased, the quantity of liquid first increases, reaches a maximum, and then after that decreases till it disappears. This is called retrograde condensation of the first kind, and has been observed by the author in the case of mixtures of methyl chloride and carbon dioxide. If P, however, lies beyond R, the process of condensation for temperatures between T_P and T_R is different. In this case the volume of vapour increases, reaches a maximum, and then decreases. This constitutes retrograde condensation of the second kind. It was with a view to the experimental observation of this second kind of retrograde condensation that the author undertook his observations. A series of observations were made with each of the pure gases, and gave the following values for the critical temperature:—

Ethane	32·3° C.
Nitrous oxide	36·1° C.

In the case of the mixtures the very interesting result is obtained that the critical temperature is in some cases less than that of either of the constituent gases. Thus a mixture containing 10 per cent of C_2H_6 has a critical temperature of 32°, the same critical temperature as for pure ethane. All mixtures containing more than 10 per cent of ethane have a lower critical temperature than 32°, the lowest critical temperature obtained being 25·8°, and corresponds to a mixture containing equal volumes of ethane and nitrous oxide. Another important point is that the border-curves do not all lie between the vapour-pressure curves of ethane and nitrous oxide. Hence for any temperature there is some mixture which gives a maximum vapour-pressure. It also appears, from the curves given in the paper, that the maximum vapour-pressure is obtained with almost the same mixture at all temperatures, and that this maximum vapour-pressure does not disappear with increase of temperature, but remains even up to the critical region.

For mixtures containing between 20 and 50 per cent of C_2H_6 retrograde condensation of the second kind takes place, but the author has not been able to observe it, since the difference between T_P and T_R for the two substances experimented on cannot be more than 0·1°, and the temperature could not be maintained sufficiently constant to hope to be able to detect any phenomenon taking place over such a small temperature range.

The author showed his arrangement for stirring the liquid and vapour in the experimental tube, so as to prevent any retardation of the different phases due to slow diffusion in the long narrow tubes employed. A small piece of iron, with enamel beads on the ends, is enclosed in the experimental tube; and by means of a small magnetising coil, which surrounds the jacket used to keep the temperature of the tube constant, this piece of iron can be moved up and down the tube so as to keep the liquid and vapour thoroughly stirred.

Prof. Carey Foster and Prof. Ramsay complimented the author on the very lucid way he had expounded a by no means easy subject.

Dr. Sidney Young congratulated the author on the able use he had made of his lucky discovery of two bodies such that their mixture should have a lower critical temperature than that of either of the pure substances. Prof. Ramsay and he (Dr. Young) had made experiments on the vapour-pressure of mixtures of alcohol and ether, and had found great difficulty in preventing the separation of the components when the volume was altered, and he could therefore thoroughly appreciate the utility of the author's device for overcoming this difficulty. They had also experienced considerable difficulty in filling the tube with a mixture of known composition and free from air, and he considered that when dealing with mixtures it was better to employ gases, although they could not be obtained in so perfect a state of purity as liquids, on account of the greater ease with which a mixture of known composition can be obtained. The plan of making separate observations on the pure substances was a good one, and, considering that the author measures the increase of pressure during the process of condensation, so that any air which happens to be present produces the maximum effect, the small rise in pressure obtained indicated a high degree of purity in the gases employed. He would like to ask the author if, in the case of mixtures, he found it possible to determine accurately the point where condensation commenced and ended, for with the alcohol and ether mixtures they had found it very difficult to determine these points. He also hoped the author would continue his observations in the direction indicated in the paper.

Mr. Inwards suggested that, in the case of liquids which act on iron, the iron stirrer could be enclosed in glass or india-rubber. It might also be possible to obtain more efficient stirring by means of a small fan or propeller worked by an electro-magnet rotating outside the tube.

Dr. Kuenen, in his reply, said that, when the mixtures were well stirred, the pressures at which condensation commenced and ended were well marked.

Mr. Burstall commenced the reading of a paper "*On the Measurement of a Cyclically Varying Temperature.*"

The experiments were undertaken with a view of measuring the temperature inside the cylinder of a gas-engine, at different points of the stroke of the piston. A modified form of platinum thermometer is employed to measure the temperature, and since the variations in temperature are extremely rapid, the wire had to be very thin and unprotected by any covering such as is ordinarily employed. The leads of the thermometer pass through a slate plug fixed in a seamless steel tube, asbestos being used as a packing to prevent leakage. The resistance of the thermometer was measured by means of a Wheatstone's bridge. Since the temperature of a certain part only of the *working* stroke had to be measured, the galvanometer circuit was broken in two places; one of these breaks was closed by means of a cam on the shaft of the engine at a given point of each revolution, while the other was closed when an explosion took place by means of a relay worked by the pointer of a steam-engine indicator attached to the cylinder of the engine.

The remainder of the paper was postponed till the next meeting.

NOTICES OF BOOKS.

Handbook of Stereochemistry. ("Handbuch der Stereochemie.") With the Co-operation of Dr. PAUL WALDEN, Tutor in Physical Chemistry. Edited by Dr. C. A. BISCHOFF, Professor of Chemistry at the Riga Polytechnicum. With 250 Figures in the Text, and Portraits of L. Pasteur, Le Bel, and J. van 't Hoff. Vol. I. Frankfurt-on-Mayn: Published by H. Bechold. 1893.

WHEN graphic formulæ were first brought into use it was erringly supposed, by not a few readers, that their object was to express the probable arrangement of the atoms in each compound. Setting aside other objections, it was at once manifest that the structure of solid bodies could not be conceivably represented on a plane surface. But we have now arrived at the concept of chemistry in space—the doctrine of geometrical isomerism, better known as stereo-chemistry. This important development of our science has hitherto scarcely received in Britain the attention to which it is entitled.

We certainly find the recognition of stereo-chemical principles in memoirs and lectures; but we have no work which presents a full view of the chemistry from the special point of view. Hence the work before us will merit, and doubtless receive, the careful attention of all students who are sufficiently versed in the German tongue.

Two shortcomings it certainly in our opinion displays; it has no table of contents, and the authors nowhere present a full view of their theories free from everything which may be regarded as scaffolding. The object of the book is to win, if possible, further adherents for stereochemistry. So rapid has been the recent progress of this region of chemistry that it becomes difficult for the student to combine the details, the ideas, and suggestions scattered in journals and pamphlets, into a general picture of the development and the present state of stereochemistry, the rather that every year is fruitful in results which have to be verified and co-ordinated with that which is already recognised.

The great proof of the value of stereo-chemistry is that it is daily leading to new experimental researches.

The authors give, in the first or general part of this book, a general view of the fundamental principles of stereo-chemistry and their historical development. They take up the work of Pasteur (1860), of Kekulé (1861—1864), and of Butlerow (1863).

Here our attention is called to the different senses which Kolbe and Gerhardt attach to the term "constitution." Like Kekulé, Gerhardt understands by "constitution" the true molecular arrangement of the atoms, whilst Kolbe believes that our researches will never lead us to a clear view of the manner in which the several atoms are respectively arranged.

The views of that epoch may be summarised as follows:—"The chemical behaviour of each atom contained in a compound molecule of any element is conditioned, on the one hand, by its nature and the chemical arrangement in the molecule, and on the other by the nature, quantity, and chemical arrangement of the other atoms contained in the same molecule."

In 1863 Carius introduced the concept of "physical isomerism."

The first attempt to represent chemical formulæ with regard to their special extension is due to Kekulé (1867).

William Thomson in 1867 published a treatise in which he maintained that the rings of Helmholtz were the only true atoms.

The first attempt to represent the position of the atoms in space is ascribed to Gustav Hinrichs, of the University of Iowa, in 1867. His views were made known in a lithographed MS. entitled "Chemistry as the Mechanics of the Panatoms."

In 1869 Paterno, in experimenting on the pentachlorinised ethan and dibrom-ethan, came to the conclusion that there was here a finer special isomerism.

In the same year Wislicenus, in his studies on lactic acid, recognised the insufficiency of structural formulæ.

In 1875 F. W. Clarke published his "Chemistry of Three Dimensions"; and in the foregoing year there appeared the memorable pamphlet of J. van 't Hoff, taking his stand on the theory of valences.

Le Bel writes, "I have succeeded, by combining the original principle of Pasteur with the discoveries of modern chemistry, in finding a simple means of foreseeing the rotatory power."

Space does not permit us to enter upon the recent researches of Fock, Wislicenus, Werner, Meyerhoffer, Vaubel, Armstrong, and other investigators.

In the second, or special, part of the work, the authors discuss the relation of the stereo-chemical theories to the optical rotatory power of organic bodies, geometrical isomerism, and the consideration of special relations in chemical reactions. Here much may be evidently expected, as we shall doubtless find in the next volume.

Might it not have been advantageous if the authors had applied their theories also to inorganic chemistry?

A Discussion of the Forces of Chemical Dynamics. ("Eine Discussion der Kräfte der Chemischen Dynamik.") Three Discourses by Dr. LUDWIG STETTENHEIMER. 8vo., pp. 88. Frankfurt-on-Mayn: Bechold. 1895.

DR. STETTENHEIMER opens his discussion by taking exception to the ordinary definition of chemistry as the doctrine of substances, their properties, and mutations. To such a definition he objects as being a more external characterisation, embracing not only a great part of pure physical processes, but in a certain respect returning to the question to be explained. Hence he takes another point of view, attacking the subject in a more abstract manner, and from the side of universal mechanics.

Thus, were chemistry fully constructed it would form, he holds, the counterpart of astronomy. "As astronomy treats of the applied, observing and describing mechanics of the greatest bodies known to us, so chemistry must be regarded as the corresponding mechanics of the minutest tissues." The author admits that this definition is not yet absolutely precise, since it does not exclude certain physical processes.

But we fear that he does not do justice to the following consideration: mechanics would be a conceivable Science if there were in the universe only one kind of matter. The problem, *e.g.*, of "three bodies" could be discussed and solved. But if there were only one element in existence chemical science could not exist, could not even be imagined! Is there not here a fundamental distinction independent of and totally other than the difference between the immeasurably large and the almost infinitely minute?

The author considers that for his theory the molecule no longer exists as a fundamental concept. In its place would come the "chemical system."

We are all well aware that Dr. Stettenheimer points out not a few flaws and shortcomings in the foundations of our Science. If he can remove what is questionable, and throw a new light upon what is doubtful, we shall hold him welcome.

It will perhaps be most serviceable to our readers if we quote the author's conclusion :—

"In electrolysis we have always obtained together the electric current and the chemical transposition in a homogeneous system, whence there have originated a series of theories to harmonise the two phenomena.

"As already shown it is the matter, *i. e.*, the atoms and groups, which arranges itself in a peculiar manner on the electric charge of a substance. We must therefore think either not at all, or only in the last place, of an electric fluid which passes over to the ions, perhaps coating them with a thin stratum, and which, by occasion of the transposition, effects the transfer of electricity. The ions are not thus electrically charged at the electrodes, but the current itself consists in the chemical transposition.

"Electricity does not play a jointly influential part in chemical transformation, but the ordinary chemical facts are not conceivable otherwise than as jointly eliciting such phenomena as the electrical. These are merely consequences of the chemical forces, and have their peculiarities only in peculiar arrangements of existing systems.

"Everything shows that there are no especial chemical forces distinct from mechanical forces; therefore, also, no molecular force different from the chemical force; no cohesive, adhesive, no electric force, for which the same does not hold good. Everything indicates the pure mechanical reciprocal action of matter (or matters?) characterised here, merely by the fact that they attach themselves in a certain manner to the minutest particles."

Theoretical and Practical Ammonia Refrigeration. A Work of Reference for Engineers and Others employed in the Management of Ice and Refrigeration Machinery. By Iltyd I. Redwood, Assoc. Member American Society of Mining Engineers; Member of Society of Chemical Industry, England. 12mo., pp. 146. New York: Spon and Chamberlain. London: E. and F. N. Spon. 1895.

Refrigeration is coming into increasing use in a variety of chemical manufactures, and, as the ammonia machine is under many circumstances the most economical and convenient, there is evidently need for the little book before us. We are sorry to find our old enemy Beaumé flourishing here in full luxuriance. Of course Twaddell, being only adapted for solutions specifically heavier than water, cannot be used for ammonia; but there can be no objection to a direct specific gravity scale, simplified by omitting the decimal point and any figure to its left hand. The explosion of a mixture of gaseous ammonia and common air is of course theoretically possible; but, after a life spent chiefly at chemical works, we must regard it as an exceptional occurrence.

The action of ammonia upon copper and its alloys is well known, and should be guarded against. But the chief danger of working with ammonia, liquid and gaseous, is the highly injurious effect upon the eyes.

The author uses the term "brine" for the watery solution of calcium and magnesium chlorides, as well as of sodium chloride. For dissolving calcium chloride the author recommends stirring or boiling. He would find it more convenient to place the lumps of the salt on a shelf covered with sacking, &c., fixed on the upper part of the bath, and thus effecting solution and filtration at one and the same time.

Mr. Redwood's recommendation to use for lubrication merely mineral oils of high viscosity is judicious, and if duly attended to will save much trouble.

CORRESPONDENCE.

ARGON IN MINERALS.

To the Editor of the Chemical News.

Sir,—We notice an extract from a letter from Dr. W. R. E. Hodgkinson in your issue of May 24 (vol. lxxi., p. 248), in which he states that he has detected argon and possibly helium in gases evolved from euxenite and samarskite when heated *in vacuo*. In reference to this we think it right to state that we have examined upwards of twenty minerals, among others samarskite and euxenite, with the view of finding a source of helium. Those which Dr. Hodgkinson has examined contain helium in small amount, and argon, if present at all, is present in exceedingly small quantity, for its spectrum is not discernible under ordinary circumstances. Indeed, we have found no mineral which gives an undoubted argon spectrum, but many which contain helium. It is impossible to conceive how Dr. Hodgkinson should have failed to see helium, for its spectrum appears in full brilliancy.

We have no desire and no right to ask Dr. Hodgkinson to discontinue his experiments, but as we should like to be allowed to publish our results *en bloc*, instead of producing them piecemeal.—We are, &c.,

W. Ramsay,
J. Norman Collie.

University College, London,
Gower Street, W.C., May 25, 1895.

"STEEL WORKS ANALYSIS."

To the Editor of the Chemical News.

Sir,—In Prof. Arnold's new work on "Steel Works Analysis," he refers to my volumetric process of determining chromium, and in introducing some modification of it offers some criticisms to which you will perhaps allow me to refer.

The modifications which he introduces seem so trivial and unusual, if not unfair, that they call, I think, for some reference or protest.

The process which he criticises was described in the Chemical News in 1877 (vol. xxxv., p. 151), while another paper on it (on account of his criticism) was read before the Iron and Steel Institute, in May, 1893, and about the same time before the Sheffield Metallurgical Society. His first objection, that chromium irons do not dissolve completely in the sulphuric acid, is a criticism which he has offered before, but the process at that time was never meant for rich chromium irons, as no such thing existed at the time. I do not know if Prof. Arnold really intends what he says on this point to be a "modification." He starts with 60 c.c. of water and 10 of sulphuric acid, as I also proposed in the original article, but states that it is necessary to boil until crystals of iron separate out, which it does after boiling about half an hour in an uncovered flask. It would scarcely be an objection, I think, to Prof. Penny's bichromate process of determining iron that some ores do not quite dissolve completely in hydrochloric acid, nor would it constitute a 'modification" to boil (and say crush the ore very fine) for an hour, supposing Prof. Penny had said half an hour.

His second objection is—

> "No precaution was given with reference to the vital-point of the vol. to which the solution must be diluted to ensure the oxidation of the chromium oxide."

In the original paper I say: "Dissolve in 6 parts of water and 1 of sulphuric acid." Prof. Arnold's modification consists in dissolving in 60 c.c. water and 10 c.c. sulphuric acid, and, after boiling till the sulphate of iron crystallises out, adding 100 c.c. water before adding the permanganate. Would not 130 c.c. water and 20 c.c.

sulphuric acid (allowing 20 c.c. for evaporation) be an equivalent?

So far as I am aware, Prof. Arnold has not shown that it is *necesssary* to dilute with this 100 c.c. water. Personally, I may say that after boiling I add some water, and will probably exceed 60 or 70 c.c. altogether, but that is done to simply add what was lost by evaporation.

How many c.c. water are necessary to constitute it a "modification"? I know some people who add 200 or 300 c.c. before adding the permanganate, and while I do not agree with them, they do not claim it as a "modification."

In his third objection, that "the amount of permanganate is six times too much," I think he is somewhat unfair. In 1877 the question was—"Would permanganate oxidise chromium oxide?" and to ensure that an excess was used. As time went on it was found that there was no fear of that, and hence an excess was not used, and the absence of any risk of non-oxidation was shown by Mr. Stead and myself in May, 1893, before the Iron and Steel Institute and the Sheffield Metallurgical Society. Yet he raises this objection in 1895. Prof. Arnold, at all events, is not entitled to any modification on this score.

Later on, Prof. Arnold writes:—"Mr. Galbraith has recently recognised this," and then he proceeds to refer to the "soda" modification which I mentioned in May, 1893. Now, this modification was introduced for irons rich in chromium, he criticises it under "Chromium Steel," for which it is quite unsuitable, and omits it under "Chromium Irons." I think I am justified, too, in saying that anything that was "recognised" here was "recognised" before Prof. Arnold "discovered" it.

I might say a very good modification of the process was described by Mr. Stead at the same two meetings referred to, and which I sometimes use, and at times think is an improvement; for instance, where there is doubt as to whether *all* the chromium is dissolved.

I really cannot think Prof. Arnold had any intention of being anything but fair in his criticism of the process, he must forgive me, however (remembering that he has twice, at all events, tried to replace it with another method, and now seems anxious that it should live), if I am anxious that it should live on its own merits and am interested in any modification of it which might be introduced.—I am, &c.,

Wm. Galbraith.

Chesterfield, May 24, 1895.

ACTION OF ARGON UPON ORGANISMS.

To the Editor of the Chemical News.

Sir,—Have you met with any systematic research on the action of argon upon living organisms, and especially upon animals? Such investigations, if existing, must have been made abroad in some country where the ruling powers are less "abhold gesinnt" to science and its followers.—I am, &c.,

J. W. Slater.

FLIES AND MICROBES.

To the Editor of the Chemical News.

Sir,—In reply to the letter appearing in the Chemical News (vol. lxxi., p. 257), I may state that I was acquainted with the article in *Nature* of March 23rd, 1893, and with the experiments mentioned by "X. Y. Z."

From all the information I had been able to gather, it appeared to me that the observers quoted by "X. Y. Z." kept their flies after contact with the pathogenic organisms in an unnatural condition, viz., *in close confinement* under glass covers. By my experiments, with harmless but easily-recognised organisms, I endeavoured to get over this important defect, and ascertain for what length of time flies would carry infection when they were allowed *perfect freedom*; and this more natural condition I endeavoured to obtain by experimenting with the flies in large furnished rooms, kept at high temperature to insure the maximum activity of the insects. For very obvious reasons it would be undesirable to experiment in this manner with flies infected with pathogenic organisms. My exhibit at the Royal Society's Conversazione was merely intended to afford a simple optical proof of the reality of the dangers which the exact and difficult researches of Sawtschenko and others have proved flies capable of causing.—I am, &c.,

William T. Burgess.

Reigate Hill, Surrey,
May 28, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 19, May 13, 1895.

Thermochemical Relations between the Isomeric States of Ordinary Glucose.—M. Berthelot.—It is concluded that in the anhydrous state the change from glucose α to glucose β would absorb $-1{\cdot}55$ cal. The change of glucose γ into glucose β would absorb $-0{\cdot}67$ cal. In the dissolved state the differences are much smaller and scarcely surpass the limits of experimental error.

On Argon and Helium.—Prof. Ramsay.—(See p. 260).

On the Definite Combination of the Copper-Aluminium Alloys.—A Rectification.—H. Le Chatelier.—The author had previously announced the extraction from alloys containing an excess of aluminium a definite compound, AlCu. He is now inclined to foresee the existence of two definite compounds, Al_2Cu and $AlCu_3$. An ingot of equal weights of the two metals having been steeped for 24 hours in a solution of sodium chloride appeared unattacked.

Determination of Sulphur in Cast Metals, Steels, and Irons.—Louis Campredon.—This paper will be inserted in full.

Researches on Mercurous Chloride, Bromide, Iodide, and Oxide.—Raoul Varet.—For the formation (setting out from the elements taken in their actual state) of mercurous chloride, bromide, iodide, and oxide, we have the following values:—

Hg_2 liq. + Cl_2 gas = Hg_2Cl_2 solution evolves $+62{\cdot}63$ cal.
Hg_2 liq. + Br_2 liq. = Hg_2Br_2 sol. $+49{\cdot}05$ cal.
Hg_2 liq. + I_2 sol. yellow amorphous $+28{\cdot}85$ cal.
Hg_2 liq. + I_2 solid greenish yellow amorphous $+28{\cdot}85$ cal.
Hg_2 liq. + O gas = Hg_2O sol. $+22{\cdot}17$ cal.

Molecular Origin of the Absorption-bands of the Salts of Cobalt and Chrome.—A. Etard.—The author concludes that—1. The salts of chrome and the red salts of cobalt present, after the manner of the rare earths and the salts of uranium, five spectral bands. 2. The spectra of these metals at least are molecular spectra like those yielded by organic matters such as the chlorophylls. 3. The hypothesis that to each band of the spectrum of a rare earth there must correspond an element is not necessarily true, as in the instance of cobalt. 4. The bands for one and the same element may be strikingly displaced or may cease to exist, according to the nature of the molecules in solution or of the compound observed.

Molecular Modifications of Glucose.—C. Tanret.—This memoir is not adapted for abstraction.

Use of Carbon Chloride as Agent for Separating Methylene from Ethylic Alcohol. — Maxime Cari-Mantrand.—The process is founded on the solubility in carbon tetrachloride, CCl_4, of the pyrogenous impurities of commercial methylenes, and on the separation of acetone and methylic alcohol mixed with vinic alcohol by distillation in presence of an alkaline chloride.

Brown Pigment in the Elytra of Curculio cupreus. —Dr. A. B. Griffiths.—The author obtains the pigment by extraction with boiling alcohol and ether. The product has the composition $C_{15}H_{13}NO$. It is soluble in alcohol, ether, and acetic acid. The solutions are gradually decolourised by light, and on spectroscopic examination do not give characteristic absorption-bands. The author names this pigment provisionally *cupreine*.

Aëration of the Soil in the Promenades and Plantations of Paris.—Louis Mangin.—The author ascribes the languid state of the ailanthus trees and the elms in and near Paris to deficient oxygenation of the soil and not to the infiltration of coal-gas.

MISCELLANEOUS.

Chemical Society in Milan.—A society has just been formed in Milan, to be known as the Societâ Chimica Milano, to be devoted to the encouragement of chemistry in all its branches.

Chemistry in Finland.—At the instance of the Academical Senate the Finnish Government has voted an annual sum of 5000 Finnish marks as the salary of a professor of chemistry at the Helsingfors University, as also an annual sum of 3000 Finnish marks in support of a hygienic laboratory. The Government has also subscribed a sum of 170,000 Finnish marks towards the cost of extending the pharmaceutical and physiological chemical laboratory.

Action of Ferric Acetate upon Potassium Iodide and Hydriodic Acid.—K. Seubert and Rud. Rohrer.—Ferric acetate and potassium iodide, either in a neutral or a strongly acetic solution, do not react in such a manner as to liberate iodine. But if free hydrochloric or sulphuric acid is added with a proportion of 3 equiv. of these acids to 1 mol. ferric acetate, in time almost the same quantities of free iodine is obtained as on the use of an equiv. quantity of ferric chloride or sulphate. The quantity of iodine ultimately set at liberty increases with the avidity of the acid present in the ferric salt.—*Zeit. Anorg. Chem.*, vii., Part 6.

Mason College, Birmingham.—Endowment of Research Scholarships. — We have received a notice concerning three "Priestley" Scholarships in Chemistry," two "Bowen" Scholarships in Engineering and one in Metallurgy, which have been founded by the late Mr. T. Aubrey Bowen, of Melbourne. They are intended to encourage and afford facilities for the higher study of these subjects in Mason College, where they are tenable for one year, with the possibility of renewal at the discretion of the Council of the College. The annual value of each is £100. Although, naturally, good work done at Mason College will be regarded as a specially favourable qualification, the Council have generously thrown all the Scholarships open to general competition. The first award will be made in September next, and all particulars may be learned on application to the Secretary of the College.

MEETINGS FOR THE WEEK.

Tuesday, June 4th.—Royal Institution, 3. "Thirty Years' Progress in Biological Science," by Prof. E. Ray Lankester, F.R.S.

Wednesday, 5th.—Geological, 8.

Thursday, 6th.—Chemical, 8. "On the Molecular Refractions of Dissolved Salts and Acids," by Dr. Gladstone, F.R.S., and W. Hibbert. "A Comparison of some Properties of Acetic Acid and its Chloro- and Bromo-Derivatives," by Spencer Pickering, F.R.S. "ββ-Dinaphthyl and its Quinones," by F. D. Chattaway, D.Sc, Ph.D.

— Royal Institution, 3. "The Instruments and Methods of Spectroscopic Astronomy," by William Huggins, D.C.L., F.R.S.

Friday, 7th.—Royal Institution, 9. "Phénomenès Physiques des Hautes Régions de l'Atmosphère," by Prof. Alfred Cornu, D.C.L., F.R.S.

— Geologists' Association, 8.

— Quekett Club, 8.

Saturday, 8th.—Royal Institution, 3. "Elizabethan Literature," by Prof. Edward Dowden, D.C.L.

Erratum.—In Mr. Aslanoglou's letter on "Test for Morphia in Urine," p. 257, col. 2, *for* "100 parts" *read* "100,000 parts of water."

THE CHEMICAL NEWS.
Vol. LXXI., No. 1854.

NOTE ON GASES OF THE HELIUM AND ARGON TYPE.

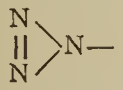
By BOHUSLAV BRAUNER, Ph.D., F.C.S.

Many years ago I obtained, on treating the mineral cerite with sulphuric acid and then with water, a gas showing the negative behaviour of nitrogen and containing some gas like hydrogen. I told this observation to Professor Ramsay two months ago, and I hope that he will not regard my experiments as a kind of trespassing on his field of investigation, especially as my experiments are only of a qualitative character. From that point of view I intended to decide the question whether helium, which is contained in clèveite—a mineral containing uranium and the rare earths—is associated with the first or the second class of substances in other minerals.

On heating the mineral cerite in a vacuum alone or with a sulphate a mixture of gases was obtained belonging, undoubtedly, to the helium and argon type, and showing in a Geissler tube a spectrum extremely rich in lines, which I shall describe fully later on. The same was observed with several Bohemian uranium ores. It is very likely that some of the cerite metals, like uranium, are elements with the highest atomic weights, and that they are found in the interior of the earth, being associated with gases of the helium and argon type.

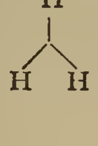
Professor Ramsay's classical research on the density of helium throws some light on the probable nature of helium and argon. Helium is, after, hydrogen, the lightest of all gases. The researches on the spectrum of helium from different sources (Lockyer) shows that it is a mixture of gases, just as argon is, and that they have one common constituent. If this common constituent is heavier than pure helium and lighter than pure argon, it is not impossible that pure helium is H_3, and pure argon N_3. It has been shown most ably by Mendeleeff that the argument derived from the relation of specific heats, $=1{\cdot}66$, is not absolutely conclusive in favour of the monoatomicity of the gases in question.

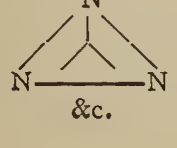
Professor Ramsay possesses important arguments against the assumption of the group—

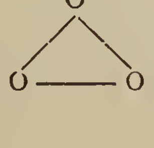


in argon, and, in fact, it is impossible, with our present ideas on "valency" and "bonds," to explain a constitution of molecules composed of "perissads" as H_3 and N_3. When we consider that Mendeleeff could write his "Principles of Chemistry" without taking "valency" and "bonds" as a basis, we shall have to look for a new mode of explanation of the constitution of the gases of the new type, before admitting that they contain new elements with the atomic weights 7·6 and 39·6, for it is highly improbable, as shown in a former note, that a new gaseous element having the boiling-point $-187°$ can be placed between chlorine and potassium.

If it should be possible to prove that helium and argon are peculiarly condensed hydrogen and nitrogen we shall have to expect a similar mode of condensation for oxygen (the group O_3 differing essentially from ozone, a peroxide of oxygen, $O=O=O$), and probably for fluorine. The constitution of the gases would then be something like the following:—







&c.

Addendum, June 2.—The gas obtained by evacuation of pitchblende (uranine) of Pribram shows a peculiar behaviour. When brought into a Geissler tube with aluminium electrodes it emits, with a feeble current, a blue-violet light; with a stronger current, a crimson light; but never the beautiful golden-yellow fluorescing glow which so much struck me when I was happily present at the discovery of helium by its spectrum, in Professor Ramsay's laboratory, on March 22nd, afternoon. With the spectroscope used, the spectroscope shows the characteristic yellow line D_3, lying a little more to the refrangible end than the double distance of D_1, and D_2 is seen distinctly, together with nineteen other lines or groups of lines, three lines belonging to hydrogen, and only one of the strong lines in the red distinctly to argon. After observing the electrised Geissler tube for some time the helium lines disappear entirely, one by one; then the hydrogen lines begin to vanish; and an extremely feeble but characteristically fluted hydrocarbon spectrum, which was hitherto invisible, makes its appearance. The fact that helium is absorbed by aluminium seems to prove its metallic character and confirm the supposition—

$$He : H = A : N.$$

CLASSIFICATION OF THE CHEMICAL ELEMENTS.

By LECOQ DE BOISBAUDRAN.

The author states at the outset that, in consequence of an oversight, he has omitted to forward the following memoir to the Secretary. But the results had, he tells us, been communicated some weeks ago to M. Friedel and M. Demarçay.

In the calculation of the atomic weights of the elements of a hypothetical family which might be introduced into the Table of Mendeleeff, forming there an eighth column, I considered in my communication to the Academy (*Comptes Rendus*, Feb. 18, 1895, p. 361) only the substance, 20·1 $(O=16)$, and its higher neighbours; that is to say, the only elements which can be introduced into Mendeleeff's eighth column, after eliminating those which rank there already, but which do not seem to me to belong to this family. Still my classification indicates the possible existence of an element ranking below the substance 20·1, with an atomic weight bordering very closely upon 3·9 $(O=16)$. Also in the family of the halogens there is room for an element below fluorine, with an atomic weight very close upon 2·9 $(O=16)$. It seems to me not useless to point out now these indications of the theory.

If we admit the real existence of the element 3·9, we are led for the substance 20·1 to an atomic weight differing but little from that which I have indicated.

I now learn that Prof. Ramsay, following up his magnificent discoveries, has determined the density of helium, referred to that of H, and finds it = 3·88. It is very remarkable that helium and argon give *for their densities* the same values which I find theoretically *for the atomic weights* of hypothetical elements which seem to agree with them.

By doubling the numbers 3·88 and 20 we should obtain atomic weights which seem difficult to place in a classification.

However, I am about to attempt here a very brief sketch of my classification, reserving for a future occasion the details and the exposition of numerous regularities, an account of which would be too tedious for this first communication.

At the outset of my researches I remarked that in each well-established natural family there exists a substance which, so to speak, summarises the characteristic properties of the family, of which it is, as it were, the centre, the *node*. I place then on the same plane the bodies of this nature, *i.e.*, Ca, K, (? δ *), Cl, S, P, Si, Al. The plane of these substances is, in fact, the upper limit of the increases of atomic weights near to 16, and the lower limit of the increases very approximately bordering on 48. Moreover, the superior triads attached to these substances are quite comparable among themselves, speaking chemically and even spectroscopically. To me the characteristic of these triads is the values of their variations, *i,e.*, the differences between the first increments bordering on 48 and the second. The values of these variations are comprised between very narrow limits.

If we place Mg and Na on the same plane as Al and Si, we compare—wrongly in my opinion—triads whose variations are very different (as well also as their chemical properties), and we then no longer find simple relations between the atomic weights of substances placed on the same plane, contrary to what holds good if we arrange the nodes as mentioned above. In this latter case we may calculate the atomic weight of a node by means of the atomic weights of the other nodes. Lastly, if we place Mg, Na, Si, P, Al, and S on the same line, we lose regularities which are useful for calculating the atomic weights of various nodes.

By means of the comparison of the variations I formerly calculated the atomic weights of gallium and germanium.

These principles lead to the following Table, considering in this preliminary paper merely the eight principal families :—

				(? η)$''$	Bi'	Pb''	Tl'	
Ba''	Cs'	(? ζ)	I'	Te''	Sb'	Sn''	In'	
Sr''	Rb'	(? ε)$''$	Br'	Se''	As'	Ge''	Ga'	
Ce''	K'	(? δ)$''$	Cl'	S''	P'	Si'	Al''	Nodes
Mg''	Na	(? γ)$''$	Fl'	O''	N	C''	Bo'	
Gl''	Li	(? β)$''$	(? α)$'$					
H	H	H	H	H	H	H	H	

All these families possess the same number of elements. The first substance of each family is derived from hydrogen.

The line of the nodes is the centre of the Table, setting out from H on the one hand, and from Bi, Pb, &c., on the other.

The nodes which have atomic weights greater than H by at least 32 may undergo two decreases of about 16 each, whence there are two substances between H on one side, and Ca, K, (? δ), and Cl on the other. The nodes which differ from H by less than 32 can undergo only one decrease of about 16, whence a simple substance between H on the one hand, and S, P, Si, and Al on the other.

But the families which have thus only a single substance below the node (H not included) receive an additional element above from the higher triad, with a large increase of atomic weight besides the highest body of the triad ; we find thus (? η), Bi, Pb, and Tl.

Setting out from hydrogen, each family therefore is formed by five successive increments, and the conditions are thus as if hydrogen itself resulted from another increment brought to a smaller element. There would be then from this hypothetical element, up to the planes Ba, Cs, ... Bi, Pb, six increments which we might suppose to correspond to the six surfaces of a cube, to the six directions of the three dimensions of space.

Recurrence, or periodicity, exists here ; it would exist, it is true, with any number of families, as if they continued to be constructed on the same plan without two great differences of increments from one plane to another.

The elements of even and odd atomicities alternate regularly from the smallest body to the largest.

The non-metals, or negative elements, occupy the centre ; the metals, or relatively positive elements, are placed at the extremities. In each of these classes the smallest element of each couple has a predominating odd atomicity ; the odd is more positive than the even, Ca'', K'—S'', P', &c.

This classification is compatible with the hypothesis that the chemical elements are in reality composed of portions of matter much smaller—far smaller even than hydrogen. This is Prout's law by extension. Provisionally, and as a maximum which I believe too high, I have adopted the $\frac{1}{128}$ of H for the unit employed in the calculations.

When once the nodes are classed according to the totality of the properties of the elements and according to the relations observed between the increments, the variations, &c., and when once the other planes are determined by the same procedure, we may thus theoretically represent the formation of the chemical elements.

Suppose a primordial mass of matter, A, which some unknown cause has just divided into two unequal portions. There will be produced on the same chemical plane two elements :—

$$\frac{A}{2} + q \text{ and } \frac{A}{2} - q ;$$

the one electro-chemico-positive in respect to the other. We have thus already a distinction between the metals and the non-metals, taking the sense of these words broadly. On splitting up anew each of these two bodies into unequal portions we obtain four elements, two of the positive and two of the negative series thus in succession. We have thus terms of transition between the most positive and the most negative elements. We confine ourselves for the present to consider eight substances thus formed. These substances, by means of successive increments or decrements, will give rise to the eight families of the foregoing Table. These increments and decrements will correspond to variations of the positive and negative characters in the perpendicular as well as in the horizontal direction of the Table. We see that the number of the families must be even.

The formation of the elements must depend therefore on the introduction of inequalities between the masses of matter, just as forces result from inequalities in the movements of bodies. In each case then is compensation, 1+ and 1− around an equilibrium which when once disturbed is never re-established. The fiction by which we may represent the formation of the elements by the unequal division of a primitive mass of matter is doubtless imaginary. Inequality must have existed from all eternity in so-called material masses, as well as in motions, by reason of a necessity always present, the cause of which escapes us. But is it not permissible for us to suppose that the material inequalities which represent the elements may be modified as do the *vires vivæ*, though their sum always remains constant ? Hitherto no satisfactory sign of a transformation of the elements, the one into the other, has been observed ; but I remain convinced that such a transformation is realised daily in Nature, under the influences of forces or of time, of which we are unable or ignorant how to avail ourselves.

By means of empirical relations, rendered very probable by their simplicity, I have sought to deduce the atomic weights of the first elements of the vertical columns from the atomic weight of hydrogen, in order to obtain absolute values for these atomic weights instead of taking for the bases of calculation the best experimental determinations. The progress of the decrements of about 16, setting out from the nodes, gives entire multiples of H, the most approximations of the atomic weights of the lower elements. The corrections to be made of these entire numbers of H follow from relations which deserve further examination, but which appear to me very simple and to agree sufficiently with the atomic weights of Li and N as determined by Stas. One of these relations would lead to the following values :—

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* An unknown body seeming to belong to the family of argon. In a second note the author enlarges on the "triads."

	H=1.	O=16.
Be	9·0156250	9·05098
Li	6·9921875	7·01961
(? β)	3·8906250	3·90588
(? α)	2·9375000	2·94902
O	15·9375000	Base
N	13·9843750	14·03922
C	11·9453125	11·99216
B	10·9218750	10·96471

Many elements may be classed according to the same principles, and following other rules the exposition of which would lead me too far. There are, however, bodies whose functions we do not know sufficiently to fix their places; we should be in danger of falling into the arbitrary.

Convinced that my attempt at classification is imperfect and incomplete, I express here the hope that it may one day experience the necessary modifications and improvements, and I shall consider myself happy if I can contribute in part to the correction of the errors almost inevitable in an investigation of this nature.

MM. Friedel and Moissan have on several occasions, and already a long time ago, heard M. Lecoq de Boisbaudran expound to them the considerations and the results which he now submits to the Academy. M. Friedel remembers having often heard M. de Boisbaudran quote, some days before the session of April 22, in which he has spoken of the atomic weights of the new elements *argon* and *helium*, the numbers 20 and 3·9 as to be probably assigned to them.—*Comptes Rendus*, cxx., No. 20, p. 1097.

THE ACTION OF HEAT UPON ETHYLENE.*

II.

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.

In a paper communicated to the Royal Society in the spring of 1894 (*Roy. Soc. Proc.*, lv., p. 90; Chem. News, lxix., p. 87), I showed that ethylene, when subjected to heat, was converted into acetylene and methane, according to the equation—

$$3C_2H_4 = 2C_2H_2 + 2CH_4,$$

and that the acetylene so formed either at once polymerised, forming a large number of secondary products, or else decomposed to carbon and hydrogen, according to the temperature at which the action was being carried on.

The fact that ethylene is one of the principal products in many cases of destructive distillation renders a knowledge of the conditions affecting these changes of considerable importance, and the experiments described in this paper were made with the view of ascertaining the effect of rate of flow, area of heated surface, and dilution upon the changes taking place.

The apparatus and methods of analysis employed were the same as described in the former paper, with the exception that a platinum tube 14 m.m. in diameter and 73·6 c.m. long, was used as the decomposing chamber, and that an easily regulated gas combustion furnace was employed as the source of heat. The temperature of the gas in the tube was measured, as before, by the Le Chatelier thermo-couple, and every precaution was taken to keep it constant during the experiments.

The ethylene in each case was prepared by heating a mixture of 25 parts, by weight, of alcohol and 150 of strong sulphuric acid, purifying, and storing in a large glass holder.

The first set of experiments was to ascertain the influence of area of heated surface upon ethylene when passing through a tube heated to the temperature most often employed in the destructive distillation of coal and hydrocarbon oils, and also to find the result of varying the rate at which the gas was passed through the zone of heat.

Table I.

Influence of Rate of Flow and Length of Heated Surface upon the Amount of Ethylene Decomposed.

Temperature, 900° C. Rate of Flow, 5 c.c. per min.

Length of tube heated.	1 inch.		6 inches.		18 inches.	
Volume of gas—						
Before heating..	525		625		625	
After heating ..	490		653		670	
Analysis of Gaseous Products.						
Carbon dioxide ..	0·75		0·50		0·75	
Oxygen	0·50		0·25		1·00	
Unsaturated hydrocarbons	17·80		10·75		2·75	
Carbon monoxide	2·21		1·75		1·75	
Saturated hydrocarbs. by absorp.	11·25	46·87	9·50	60·75	12·22	65·42
Do. by explos.	35·62		51·25		53·20	
Hydrogen	24·12		22·75		24·00	
Nitrogen	7·75		3·25		4·33	

On now calculating the percentage for the change in volume, we obtain the following figures:—

Length of tube heated.	1 inch.	6 inches.	18 inches.
Unsaturated hydrocarbons	16·60	11·25	2·94
Saturated hydrocarbons	43·72	63·42	70·13
Hydrogen	22·50	23·75	25·72

The original gas, however, only contained 96·7 per cent of ethylene, so that the percentage of unsaturated hydrocarbons decomposed are:—

Length of tube heated.	1 inch.	6 inches.	18 inches.
	80·1	85·48	93·76

Table II.

Temperature, 900° C. Rate of Flow, 15 c.c.

Length of tube heated.	1 inch.		6 inches.		18 inches.	
Volume of gas—						
Before heating..	683		600		600	
After heating ..	615		515		640	
Analysis of Gaseous Products.						
Carbon dioxide ..	0·20		1·00		0·50	
Oxygen	0·50		0·50		0·75	
Unsaturated hydrocarbons	28·75		20·15		6·00	
Carbon monoxide	1·50		1·50		1·75	
Saturated hydrocarbs. by absorp.	8·80	42·25	9·43	51·81	19·22	56·72
Do. by explos.	33·45		42·37		37·50	
Hydrogen	21·15		20·55		28·75	
Nitrogen	5·65		4·50		5·53	

On now calculating the percentage for the change in volume, we obtain the following figures:—

Length of tube heated.	1 inch.	6 inches.	18 inches.
Unsaturated hydrocarbons	25·87	17·28	6·39
Saturated hydrocarbons	38·02	44·44	60·46
Hydrogen	19·03	17·63	30·64

The original gas contained 96·7 per cent of ethylene, so that the percentages of unsaturated hydrocarbons decomposed are—

Length of tube heated.	1 inch.	6 inches.	18 inches.
	70·83	79·42	90·31

(To be continued.)

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* A Paper read before the Royal Society.

ON THE

ESTIMATION OF CYANOGEN IN IMPURE SOLUTIONS, PARTICULARLY THOSE CONTAINING ZINC.

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It is a common complaint among those who have to do with the extraction of gold by the cyanide process, that the amount of cyanide in a given solution cannot be accurately determined, owing to the presence of various impurities in suspension or solution. The indications by the ordinary method of titration with silver nitrate are both indefinite and erroneous. Various suggestions have been made for overcoming this difficulty. As the matter is one of considerable technical importance, we thought it worth while to make an examination of some of the proposed methods. Those which we shall describe are—

1. Preliminary treatment with lime.
2. Titration with iodine.
3. Precipitation of the impurities by alkaline sulphides.

A. *Preliminary Treatment with Lime.*

Solutions are frequently met with containing exceedingly fine matter in suspension, which cannot be rendered clear even by repeated filtration. Such solutions are frequently treated by agitation with caustic lime, which causes a deposition of the suspended matter in a flocculent condition, in which state it can be readily removed by filtration. Lime has practically no action on alkaline cyanides; but there is of course a small error introduced, owing to the change of volume due to the dissolved lime. This, however, is negligible.

This method was found to yield accurate results only when the solution contained no soluble double cyanides. It may be employed with advantage when the liquid is turbid from the presence of finely-divided silica, oxide of iron, alumina, or other inert substance in suspension. Some double cyanides, such as that of zinc and potassium, are partially decomposed with precipitation of hydrate, $K_2ZnCy_4 + Ca(OH)_2 = Zn(OH)_2 + 2KCy + CaCy_2$, but the reaction is never complete. The indications obtained after such treatment are valueless, because, although the addition of caustic alkalies sets free some of the combined cyanide, and so raises the apparent strength of the solution, it does not enable us to determine the total amount of cyanogen. In solutions containing zinc the end-point is always preceded by the appearance of the characteristic flocculent precipitate of zinc cyanide ($ZnCy_2$).

Two solutions from the "zinc boxes" were tested, with the following results:—

(The silver nitrate solution was of such a strength that 1 c.c. = 0·01 grm. KCy.)

No. 1.

	Without lime.	With lime.
First turbidity with $AgNO_3$, 25 c.c. taken for test ..	0·9 c.c.	1·05 c.c.
Indicated strength	0·036 p. c.	0·042 p. c.

No. 2. 20 c.c. taken for each test.

	$AgNO_3$ required for first turbidity.	Indicated strength.
Without lime	0·4 c.c.	0·02 p. c.
With 0·1 grm. lime ..	1·5 ,,	0·075 ,,
,, 0·5 ,, ..	2·0 ,,	0·1 ,,
,, 1·0 ,, ..	2·0 ,,	0·1 ,,

B. *Titration with Iodine.*

Turbid solutions, if free from zinc, may in many cases be accurately titrated, without filtering, by the method of Fordos and Gelis. A solution of iodine in iodide of potassium is standardised against a solution of pure potassium cyanide, the strength of which has been accurately determined by the silver nitrate method. The end-point of the iodine reaction is marked by the appearance of a permanent yellow tint, or, if starch has been added, of a bluish-violet colour, and is in general very sharp and delicate. It is essential, however, that the solution shall contain no free caustic alkali or alkaline monocarbonate, as these bodies react with iodine, rendering the indications too high and also indefinite. It is generally recommended (see Sutton, "Vol. Anal.," 7th ed., p. 175) to remove the excess of alkali by the addition of soda-water (*i. e.*, a solution of carbonic acid); but this is troublesome, since any excess of carbonic acid will decompose cyanide with evolution of hydrocyanic acid.

The following simple method was found by the writer to give accurate results:—

Silver nitrate is first added to a measured volume of the solution to be tested until a permanent turbidity, or, if the solution was originally turbid, a distinct increase of turbidity, is observed. Addition of a few drops in excess is of no consequence. A drop of phenolphthalein indicator is now added to the same liquid, and the titration is continued with N/10 hydrochloric acid, until the pink colour disappears. Another measured portion of the original solution is then taken, and a trifle less than the quantity of hydrochloric acid shown to be necessary by the previous experiment for neutralisation of the alkali is added, drop by drop, with agitation. The solution is now ready for titration with iodine.

This process depends upon the following considerations:—

1. In a mixture containing alkaline cyanides, hydrates, and monocarbonates, the hydrates are converted into neutral salts, and the monocarbonates into bicarbonates, by the addition of a dilute mineral acid, before any of the cyanides are decomposed.
2. Bicarbonates of the alkali-metals are without action upon iodine.
3. When the cyanide in such a mixture has been converted into a double silver salt, the titration with dilute hydrochloric acid, with phenolphthalein as indicator, indicates the quantity required to neutralise the hydrates and convert the carbonates into bicarbonates (see Chem. News, Feb. 22, 1895).

The following experiments illustrate the effect of caustic alkalies on the indications by the iodine method of titration:—

No. of Expt.	Vol. of 0·05 p.c. KCy.	Vol. of N/10 KOH added.	Vol. of Iodine required.	Indicated strength of KCy.	Remarks. (1 c.c. Iodine = 0·0035 grs. KCy.)
1	10 c.c.	—	1·4 c.c.	0·049 %	End-point quite definite.
2	10 ,,	5 c.c.	1·6 ,,	0·056 ,,	,, indefinite.
3	10 ,,	10 ,,	1·9 ,,	0·066 ,,	,, ,,
4	10 ,,	15 ,,	?	?	Faint yellowish tint beginning, about 1·6 c.c. End of reaction quite impossible to determine.

The effect of neutralising the alkali by the addition of hydrochloric acid is shown by the following experiments:—

A. A mixture of pure cyanide and caustic potash was prepared.

a. 10 c.c required 3·7 c.c. standard iodine, the end-point being somewhat indefinite.

b. 10 c.c. required 1·15 c.c. standard silver nitrate. On adding phenolphthalein and titrating with N/10 hydrochloric acid 5·75 c.c. were required.

c. 10 c.c. were mixed gradually with 5·5 c.c. of N/10 hydrochloric acid and the mixture titrated with iodine. 3·3 c.c. were required, the end-point being quite sharp.

d. 10 c.c. were mixed gradually with 5·5 c.c. of N/10 hydrochloric acid, and the mixture titrated with standard $AgNO_3$. 1·15 c.c. were required.

In these experiments—

1 c.c. standard $AgNO_3$ solution = 0·01 grm. KCy
1 ,, ,, iodine ,, = 0·0035 ,,

Hence the calculated percentage of cyanide in the four experiments above is as follows:—

a	0·1295 per cent
b	0·1150 ,,
c	0·1155 ,,
d	0·1150 ,,

B. An impure solution was titrated with the following results:—

a. 10 c.c. titrated with $AgNO_3$ gave a faint indication of turbidity with 1·6 c.c., distinct turbidity with 1·9 c.c. (indicating 1·6 per cent—0·19 per cent KCy).

b. 10 c.c. titrated direct with iodine required 6 c.c. (indicating 0·21 per cent KCy).

c. 10 c.c. were taken and 2 c.c. $AgNO_3$ added. This mixture was titrated with N/10 hydrochloric acid, using phenolphthalein indicator. 1·7 c.c. were required.

d. 10 c.c. were taken, and 1·5 c.c. N/10 hydrochloric acid added. This solution was then titrated with iodine, 5·95 c.c. being required (indicating 0·208 per cent KCy).

C. A mixture of cyanide and carbonate gave the following results:—

a. 25 c.c. required 1·1 c.c. $AgNO_3$ to give a permanent turbidity (indicating 0·044 per cent KCy). On continuing the titration with N/10 hydrochloric acid 4·6 c.c. were required.

b. 25 c.c. were taken, and 4·5 c.c. N/10 hydrochloric acid added. This mixture required 1·1 c.c. $AgNO_3$ (indicating 0·044 per cent KCy).

c. The same mixture required 3·65 c.c. iodine (1 c.c. iodine = 0·00323 grm. KCy). The indication, therefore, represents 0·047 per cent KCy.

D. Another mixture of cyanide and carbonate gave the following results:—

	No. of test.		
	1.	2.	3.
	C.c.	C.c.	C.c.
Volume of mixture taken	25	25	25
Volume of N/10 hydrochloric acid added	—	16	16
Volume of standard $AgNO_3$ required	1·0	1·05	—
Volume of standard iodine required	—	—	3·0
Indicated percentage of KCy ..	0·04	0·042	0·039

Test No. 1 was titrated with N/10 hydrochloric acid after addition of $AgNO_3$. 16 c.c. were required to destroy the phenolphthalein colour.

Solutions containing zinc did not give satisfactory results when titrated with iodine. In the first stage of the titration a faint yellowish tint appears in the solution, which is succeeded by a white flocculent precipitate. The first appearance of this precipitate was generally difficult to detect, but, in some instances at any rate, it appeared to correspond with the formation of a similar precipitate when silver nitrate is used, and therefore probably indicates the completion of the reaction—

$$KCy + I_2 = KI + ICy,$$

and the commencement of the decomposition of the double cyanide according to the equation—

$$K_2ZnCy_4 + 2I_2 = 2KI + 2ICy + ZnCy_2.$$

After the formation of this precipitate the solution becomes colourless. On further addition of iodine, the amount of the flocculent precipitate continually increases until, at a certain stage, also very indefinite, the yellow colour reappears. The following results were obtained in testing various solutions containing zinc by both methods:—

	Percentage of KCy indicated.		
		By Iodine.	
No. of test.	By $AgNO_3$. First precipitate.	First precipitate.	Permanent yellow tint.
1. Weak solution ..	0·026	0·026	0·142
2. ,, ,, ..	0·036	0·035	0·079
3. Strong solution ..	0·260	0·232	0·283
4. ,, ,, ..	0·275	0·238	0·312
5. ,, ,, ..	0·275	0·240	0·310

C. *Precipitation by Alkaline Sulphides.*

The methods given in the various text-books for estimating cyanogen in double cyanides are, as a rule, tedious, and involve a number of separate operations, some of which occupy a considerable amount of time. The following method, while it is not applicable to every possible case, is fairly rapid, and serves to determine the "total cyanide" (*i.e.*, the whole of the cyanogen, estimated as its equivalent of potassium cyanide) in solutions commonly met with, particularly such as contain zinc. It depends upon the following facts:—

1. That many double cyanides, such as those of zinc, silver, mercury, &c., are decomposed by sulphuretted hydrogen or an alkaline sulphide, with precipitation of the metal as sulphide (see Valentine, "Qual. Anal.").

2. That the excess of sulphide may be removed without affecting the cyanides by the addition of insoluble compounds of lead, such as the oxides, carbonate, &c. (see Fresenius, "Quant. Anal.," vol. i., p. 375).

The method is as follows:—A measured volume of the solution is made strongly alkaline by the addition of caustic potash or soda. Sulphuretted hydrogen is passed into the liquid until it ceases to give a precipitate, avoiding a large excess, or, which is better, a concentrated solution of pure sodium sulphide is added in slight excess. The solution is then well shaken and allowed to stand until the precipitate has subsided. A little lime may be added to assist the settling of the precipitate, in which case it can be filtered without difficulty. The clear filtrate is freed from excess of sulphide by agitating with litharge, which is best added in small quantities at a time, with constant agitation, until a drop of the liquid no longer gives the slightest black or brown colouration with a drop of lead acetate solution. A definite volume is then filtered off, and tested with silver nitrate in the ordinary manner.

Another method (which is not perfectly accurate, as the volumes occupied by the precipitated sulphides, and the excess of lead carbonate are neglected) is as follows. It is accurate enough for most practical purposes:—After precipitation with sulphuretted hydrogen or sodium sulphide, the liquid is made up to a definite volume, say 100 c.c., and, after settling, a measured volume of the clear liquid (say, 50 c.c. or 25 c.c.) is taken, and added, with agitation, to a freshly prepared mixture of lead acetate and sodium carbonate, in which an excess of sodium carbonate is present. Sufficient lead must be present (as carbonate) to convert the excess of sodium sulphide into lead sulphide and sodium carbonate. The liquid is again made up to a definite volume and allowed to stand. The precipitate settles very rapidly, and a definite volume of the supernatant liquid is decanted off; filtering if necessary. This may now be tested with silver nitrate.

The liquid to be tested must fulfil the following conditions:—

1. It should give a perfectly white precipitate with a drop of lead acetate solution.
2. It should give no precipitate with sodium carbonate.
3. It should give no precipitate with sulphuretted hydrogen. A faint brown colouration is usually produced, probably owing to the solution of a small quantity of lead oxide or carbonate in the alkaline fluid.

In titrating with silver nitrate a slight granular precipitate was generally observed towards the finish. It was necessary to add the last few drops of silver nitrate slowly, with agitation. The end-point, however, was perfectly definite, the granular precipitate being disregarded. The point to be noted is the appearance of a distinct permanent turbidity pervading the whole liquid and not disappearing on standing.

The following experiments will illustrate the application of the method:—

a. A mixture was made of—
25 c.c. pure potassium cyanide (KCy=0·924 p.c.)
* 2 ,, zinc sulphate (1 c.c. = 0·01 grm. Zn)
10 ,, normal caustic potash
10 ,, concentrated sodium carbonate.

This mixture was precipitated by sulphuretted hydrogen, and the precipitate filtered off and washed thoroughly. The filtrate was mixed with sufficient lead acetate solution to precipitate the excess of sulphide, and made up to 100 c.c.

25 c.c. required 5·7 c.c. standard $AgNO_3$
" " 5·7 " "
Indicating 0·912 per cent KCy.

b. A mixture was made of—
50 c.c. pure potassium cyanide (KCy=0·924 p.c.).
10 c.c. pure zinc sulphate (1 c.c.=0·01 grm. Zn).
10 c.c. normal caustic potash.
10 c.c. concentrated sodium carbonate.

After passing in sulphuretted hydrogen, the liquid was made up to 100 c.c, After allowing the precipitate to settle, the supernatant liquid was filtered, and 25 c.c. of the clear filtrate were added to a mixture of lead acetate with excess of sodium carbonate. This was made up to 100 c.c. and filtered.

50 c.c. required 5·65 c.c. standard $AgNO_3$.
Indicating 0·904 per cent KCY.

c. A mixture was made of—
40 c.c. pure potassium cyanide (KCy=0·924 p.c.).
5 c.c. pure zinc sulphate (1 c.c.=0·01 grm. Zn).
20 c.c. normal caustic soda.

This was precipitated by sulphuretted hydrogen, diluted to 100 c.c., and agitated with a little caustic lime. After the precipitate had settled, 25 c.c. of the clear liquid were added to a mixture of lead acetate and potassium carbonate, in which the alkaline carbonate was in excess. The liquid was made up to 100 c.c. and filtered.

25 c.c. of the filtrate required 2·4 c.c. standard $AgNO_3$.
50 c.c. ,, ,, 4·75 c.c. ,, ,,
Indicating 0·955 per cent KCy.

d. A mixture was made of—
40 c.c. pure potassium cyanide (KCy=0·924 p.c.)
5 c.c. pure zinc sulphate (1 c.c.=0·01 grm. Zn).
20 c.c. normal caustic soda.

This mixture was precipitated with sulphuretted hydrogen, and the liquid diluted to 100 c.c. One grm. of caustic lime was added, and, when the precipitate had settled, 50 c.c. of the clear liquid were agitated with 25 grms. of litharge. The solution was then filtered.

25 c.c. required 9·35 c.c. $AgNO_3$.
25 c.c. ,, 9·25 c.c. ,,
Indicating 0·93 per cent KCy.

e. A mixture was made of—
40 c.c. pure potassium cyanide (0·924 per cent).
5 c.c. pure zinc sulphate (1 c.c.=0·01 grm. Zn).
20 c.c. normal caustic soda.

To this was added 5 c.c. of a concentrated solution of pure sodium sulphide, the liquid made up to 100 c.c., and settled with lime; 25 c.c. of the clear liquor were added to a mixture of lead acetate with excess of potassium carbonate. This was made up to 100 c.c. and filtered.

25 c.c. required 2·4 c.c. $AgNO_3$.
50 c.c. ,, 4·65 c.c. ,,
Indicating 0·945 per cent KCy.

Whenever the quantity of zinc was at all considerable it was found necessary—

1. To remove the precipitated zinc sulphide by filtration before addition of lead salts. (Even thoroughly washed sulphide of zinc reacts upon carbonate of lead with formation of lead sulphide).
2. To add an insoluble compound of lead, and not a solution of lead acetate. The latter would be liable to precipitate cyanide of lead.

Before precipitating with sulphuretted hydrogen it is necessary to add a considerable quantity of alkaline hydrate, or low results will be obtained, owing to the liberation of hydrocyanic acid. When an alkaline monocarbonate was substituted for the hydrate the results were not satisfactory.

Application of the Method to Solutions from the Zinc-boxes.

The solution tested had been used for fifteen successive washes on the same charge of material, and had been passed each time through the zinc-boxes. It was therefore highly charged with zinc, as well as various impurities extracted from the ore.

(*a*). Tested by direct titration with silver nitrate, 10 c.c. required 1·45 c.c. $AgNO_3$ to give the first sign of a permanent turbidity (indicating 0·145 per cent), and 1·7 to to 1·8 c.c. to give a perfectly distinct turbidity. The "free cyanide" may therefore be taken as about 0·17 to 0·18 per cent.

(*b*). The same solution was tested in a variety of ways for "total cyanide," by the method described above. The following mixtures were made:—

	(i.)	(ii.)	(iii.)
Solution taken	40 c.c.	80 c.c.	40 c.c.
Normal caustic soda	20 ,,	10 ,,	10 ,,
Precipitant used ..	H_2S	H_2S	Na_2S
Indicated strength in KCy..	0·80 p.c.	0·77 p.c.	0·785 p.c.

Mean of all determinations, 0·789 per cent.

In each case the excess of sulphide was removed by means of a mixture of lead acetate with excess of potassium carbonate.

In a future paper I hope to be able to give particulars of a method successfully applied here for estimating cyanides and ferrocyanides in the same solution.

Johannesburg, April 16, 1895.

The late Prof. Neumann.—We regret to record the death of Geh. Rath. Neumann, Professor of Physics at the University of Königsberg, Prussia, at the advanced age of 97. Prof. Neumann was born in 1798, at Joachimsthal, near Berlin, and studied at Jena and Berlin. He became connected with the University of Konigsberg in 1826. His chief researches were in connection with specific heat, polarisation of light, and magnetism and electricity.

New Edition of "Bloxam's Chemistry."—Messrs. J. and A. Churchill announce a new edition, re-written and revised, of "Bloxam's Chemistry, Inorganic and Organic," by Prof. J. M. Thomson, of King's College, and Mr. A. G. Bloxam, Head of the Chemistry Department, Goldsmith's Institute. Several new woodcuts have been added. The same firm also announce as nearly ready a new work by Mr. Alfred H. Allen, entitled "The Chemistry of Urine, a Practical Guide to the Examination of Diabetic, Albuminous, and Gouty Urine," with illustrations.

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* Assuming that 1 part of zinc is capable of converting 4 parts of KCy into the double cyanide (K_2ZnCy_4), this solution should contain the equivalent of 0·08 grm. KCy as K_2ZnCy_4 and 0·151 grm. free KCy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 16th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Croysdale, The Grange, Whitley Bridge, R.S.O.; Joseph Lones, Lansdowne, South Road, Smethwick; Arthur E. Potter, M.A., B.Sc., Rangoon; E. J. Read, B.A., 2, Leigh Terrace, Bedford.

The following were duly elected Fellows of the Society:—Harold Allden Auden, B.Sc.; Edgar S. Barralet; Eugen Blume; Lancelot Alexander Borradaile, B.A.; Henry Bradford; Gustav Theodore Bruckmann, B.Sc.; Walter W. Cheadle, B.A.; Virgil Coblentz, Ph.G., A.M., Ph.D.; Herbert William Cook, B.Sc.; Edric Druce; Arthur T. Eutroppe; Sydney Fawns; Hasslewood Irving Foster; Alexander F. Fuerst, Ph.D.; John Francis Hutchins Gilbard; William Goddard; Patrick Hope Grant; William Abraham Greaves, B.Sc.; Alexander Gunn; H. Loft Haller; Evan Lewis Jones, B.A.; Robert Charles Marchant; Prosper Henry Marsden; John McGlashan; Robert Selby Morrell, M.A., Ph.D.; Charles Butterworth Newton; Lama Gray Patterson; George Elliott Shaw; Frank L. Slocum; Kekhasrie Engineer Sorabji; Thomas Coke Squance, M.D., M.S.; Alfred Stansfield, B.Sc.; Alfred F. Theodosius, B.A.; William Thomas Thomson; Arthur Thornton, M.A.; Frederick Gwilym Treharne; George John Ward; Arthur William Warwick; Henry F. A. Wigley, B.A.; William Arthur Whiston; John Wilson, B.Sc.

Of the following papers those marked * were read:—

*65. "*Kjeldahl's Method for the Determination of Nitrogen.*" By BERNARD DYER, D.Sc.

This method, variously modified, has, in most agricultural laboratories, superseded the well-known soda-lime method, over which it possesses marked advantages for the analysis of feeding-stuffs and fertilisers. It has not, however, been generally adopted by scientific chemists, and little information is available as to its applicability to different types of organic compounds. To supply such information was the object of the present investigation.

The best modification of the method, in the author's experience, for the analysis of feeding-stuffs and fertilisers not containing nitrates, and applicable, as will be seen, to a large number of organic compounds, is the Kjeldahl-Gunning method modified, however, by the use of mercury. A suitable quantity of the material to be analysed is mixed in a round-bottomed, hard glass flask, with 20 c.c. of strong sulphuric acid and a drop of mercury, and warmed for a short time, when 10 grms of potassium sulphate are added. The contents of the flask are then boiled until colourless. With many materials this result happens within half an hour, and it is rarely deferred beyond an hour. The contents are washed into a distilling flask, mixed with excess of soda and a little potassium sulphide (to decompose mercury compounds), and the ammonia then distilled off into standard acid, which is afterwards titrated in the usual way. No spray trap is necessary in distilling if the connection between the distilling flask and receiver is made by means of a long block-tin tube, rising perpendicularly 15 or 20 inches from the neck of the flask. The author prefers not to use a condenser, but to drive the steam directly into the standard acid, which stands in a trough of cold water, the delivery tube terminating in a pear-shaped glass bulb, to prevent regurgitation of the acid. The use of mercury is not necessary, but materially expedites the process.

When nitrates are present, or nitro-compounds and certain other compounds referred to in the paper, Jodlbauer's modification is used. This consists in dissolving in the sulphuric acid used for oxidation a small quantity (about 2 grms. for a single determination) of phenol or salicylic acid. The nitrogen in the nitrate or nitro-group then forms a nitro-compound with the sulphonated phenol or salicylic acid. In many cases it is highly important that the sulphuric acid containing the phenol or salicylic acid should be poured directly and suddenly on to the material contained in the flask, so as to submerge it immediately, and not to let it trickle from a pipette. If nitrates and ammonium salts are both present, loss of nitrogen occurs, unless this precaution is observed; this does not appear to be generally known, and probably often gives rise to errors. One or two grms. of zinc dust (as well as a drop of mercury) are dissolved in the contents of the flask while still cold. The process is then continued exactly as before.

The method first described as the "Kjeldahl-Gunning" method was found to give very nearly the exact percentages of nitrogen in uric acid, asparagine, caffeine, indigotine, morphine, quinine, strychnine, aniline, atropine, diphenylamine, naphthylamine, acetanilide, orthobenzoic sulphinide, sulphamido-benzoic acid, pyridine, benzidine, aldehyde ammonia, and nitroso-di-methyl-aniline.

The Jodlbauer modification referred to by the author as the "Kjeldahl-Gunning-Jodlbauer" method, was found to give nearly correct percentages of nitrogen in potassium nitrate, ammonium nitrate, urea nitrate, nitrobenzene, nitronaphthalene, nitraniline, dinitrobenzene, trinitrophenol, and potassium para-bromo-chlor-nitro-phenol.

It might be expected that reduction with zinc alone, without the use of phenol or salicylic acid, would suffice in the case of aromatic nitro-compounds. The author finds, however, that if zinc alone be used with aromatic nitro-compounds there is loss of nitrogen, as though it were necessary that more carbon should be present.

The Kjeldahl-Gunning method fails to furnish the calculated quantity of nitrogen in azobenzene or amido-azobenzene. The loss in the former case was small; in the latter case it amounted to nearly 50 per cent. Mere reduction by zinc suffices with amido-azobenzene, but in the case of azobenzene the complete Jodlbauer modification is necessary. With amido-azotoluene the correct amount was obtained by the Kjeldahl-Gunning process supplemented by reduction with zinc and with carbazol by the Kjeldahl-Gunning method alone.

Hydroxylamine hydrochloride, which contains 20·21 per cent of nitrogen, yielded only 3 per cent by the Kjeldahl-Gunning method; by reduction with zinc about 10 per cent was obtained; by the Kjeldahl-Gunning-Jodlbauer method about 19 per cent; by reduction with sugar and zinc less than 19 per cent. The Kjeldahl-Gunning-Jodlbauer method, with the addition of sugar as well as zinc, however, gave the calculated quantity in each of three separate determinations. Acetaldoxime, by the Kjeldahl-Gunning method, gave somewhat low results, but with the addition of sugar and zinc furnished correct results. Naphthoquinone-oxime yields its full percentage by the Kjeldahl-Gunning method.

Potassium cyanide and ethyl cyanide both give nearly correct results by the Kjeldahl Gunning method; no trace of hydrocyanic acid is evolved if the sulphuric acid used is strong. Potassium ferrocyanide also yields accurate results. Potassium ferricyanide, however, only gives sufficiently accurate results when reduced by the addition of sodium thiosulphate. Sodium nitroprusside failed with any modification of the method to yield all its nitrogen.

Phenyl-hydrazine derivatives cannot by any modification of the method tried by the author be made to give correct results; there is invariably loss of nitrogen, presumably liberated in the free state. The derivatives used were phenyl-hydrazinehydrochloride and glucosazone. Symmetrical di-phenyl hydrazine, or hydrazobenzene, affords accurate results with the Kjeldahl-Gunning method. This substance, however, ceases to be a hydrazine when dissolved in acid, as it is converted into benzidine which furnishes the calculated amount of nitrogen.

Discussion.

Dr. **Kipping** remarked that Dr. Dyer's results pointed to the conclusion that different types of organic compounds required special treatment in order to obtain the whole of the nitrogen as ammonia, whilst some compounds did not under any conditions furnish accurate results. The method could not therefore be regarded as a substitute for the absolute method of Dumas.

Mr. **Hehner** said that few analytical processes had been the subject of so much investigation as the Kjeldahl method, the original process having undergone very many modifications. Originally the oxidation was carried out only very partially by sulphuric acid, potassium permanganate being used as soon as the acid had produced charring. Kjeldahl had found that by the action of the acid alone only about 25 per cent of the total nitrogen in quinine, and about 40 per cent of the nitrogen in morphine, was obtained, whilst after the action of permanganate almost the whole of the nitrogen appeared as ammonia. The use of permanganate had already been recognised as leading to the loss of nitrogen, and Kjeldahl had himself pointed out that the heating after the addition of permanganate must be moderate, or loss may occur. Much of the ground occupied by Dr. Dyer's paper had already been gone over by others, especially by Arnold and Wedemeyer. Taking into account the results obtained by the various investigators of the process, it might be said that the Kjeldahl process, as modified by Wilfarth, Gunning, and Jodlbauer, was a most accurate and convenient one for the determination of nitrogen in naturally occurring nitrogenous substances, especially in feeding materials.

Dr. **Morris** considered that there was no doubt as to the value of Kjeldahl's process for determining nitrogen in proteids and similar nitrogenous compounds. He had found it advantageous to use permanganate as originally suggested by Kjeldahl.

Professor **Dunstan** suggested the stability of hydroxylamine sulphate as a probable explanation of the small amount of ammonia furnished by hydroxylamine salts in the absence of a special reducing agent. The subsequent action of alkali on the sulphate would liberate only a part of the nitrogen as ammonia. Similarly with oximes, some hydrolysis would occur, producing hydroxylamine sulphate, although here the decomposition of the hydrocarbon radicle would ensure nearly complete reduction of the oximido-group to ammonia.

*66. "*Note on Liquation in Crystalline Standard Gold.*" By T. K. **Rose**, D.Sc., A.R.S.M., Assistant Assayer of the Royal Mint.

It has been suggested by Roberts-Austen that, although no segregation occurs on the solidification of alloys of gold with silver and copper, some rearrangement might be expected to take place when these alloys are made crystalline and brittle by the addition of small quantities of bismuth or lead. The author accordingly rendered standard gold impure in three successive experiments by the addition of 0·2 and 0·4 per cent of bismuth and 0·2 per cent of lead respectively, casting the metal in a spherical iron mould, and assaying various parts of the mass.

The observed variations in the composition of different parts of the mass can be explained by assuming that in these alloys a saturated solution of gold and silver in bismuth or lead (no doubt containing a little copper in addition) remains molten after the greater part of the gold and copper has solidified. Those constituents which are the first to become solid are thus enabled to assume a definite crystalline form. Moreover, as the portion of the material which remains molten longest is pushed towards the centre of the mass during cooling, the interior is enriched in both gold and silver.

*67. "*Preparation of the Active Lactic Acids and the Rotation of their Metallic Salts in Solution.*" By T. **Purdie**, Ph.D., B.Sc., and J. **Wallace Walker**, M.A.

The authors have prepared the active lactic acids in considerable quantity by the process previously described (*Trans.*, 1893, lxiii., 1143), using certain modifications, and have used the material thus obtained for examining the optical activity of some of the metallic lactates in aqueous, alcoholic, and aqueous-alcoholic solutions of varying equivalent concentrations. The freezing-points of a number of the same solutions were also determined with the double object of obtaining an approximate estimate of the amount of dissociation attending the changes in molecular rotation, and of detecting the existence or non-existence of racemoid compounds in solution.

The salts examined were those of lithium, sodium, potassium, silver, calcium, strontium, barium, magnesium, zinc, cadmium, and zinc-ammonium.

All these salts in aqueous solution within the limits of concentration used were found to be active in the opposite sense to that of the acid from which they were prepared, and the activity was found to increase with dilution, except in the case of the silver salt, the rotation of which undergoes a slight decrease.

The salts of the alkaline metals comprising those of silver, also those of barium and strontium, tend to a common maximum molecular rotation of about 14·5°, an observation which is in accordance with the law of Oudemans. The salts of the other metals show divergencies from this law which indicate that the activity of their solutions cannot be accounted for by the presence of simple molecules and ions alone, but that it is probably largely influenced by the formation of molecular aggregates, whose activity differs widely from that of the other factors. This assumption is confirmed by observations of the rotation of the sodium and potassium lactates in alcohol and of other salts in aqueous alcohol.

A comparison of the freezing-points of solutions of active and inactive lithium and strontium lactates shows that the racemoid salts are resolved into their components in aqueous solution. The corresponding coefficients of depression of the barium salts show slight differences which may possibly be due to the presence of racemoid salt.

68. "*Derivatives of Succinyl and Phthalyl Dithiocarbimides.*" By **Augustus E. Dixon**, M.D., and **R. E. Doran**.

On heating together lead thiocyanate, succinyl chloride, and dry benzene, succinyldithiocarbimide is formed and goes into solution,—

$$C_2H_4(COCl)_2 + Pb(SCN)_2 = PbCl_2 + C_2H_4(CO{\cdot}NCS)_2.$$

It is a pungently smelling, very unstable compound, soluble in all proportions in benzene, decomposed by water into succinic and thiocyanic acids, and easily desulphurised by silver or alkaline lead salts.

The benzene solution yields, on the addition of bases, the corresponding symmetrical dithioureas. From aniline, *succinyldiphenyldithiourea* was obtained,—

$$C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NHPh)_2.$$

This forms silky needles (from hot acetic acid), sparingly soluble in most solvents, and melting with decomposition at 210—210·5° (corr.). The compound is readily desulphurised by ammoniacal silver nitrate in the cold, or by warming with alkaline lead tartrate. It dissolves in warm dilute caustic alkali, thereby breaking up into phenylthiourea and succinic acid; and is decomposed by alcoholic ammonia, under pressure, forming phenylthiourea.

Succinyldiorthotolyldithiourea,—

$$C_2H_4(CO{\cdot}NH{\cdot}CS{\cdot}NH\textit{o}\text{-}To),$$

similarly prepared from *o*-toluidine (yield = 96 per cent), formed colourless glassy needles, melting at 217—218°, and resembling in most other respects the corresponding phenyl compound.

Succinyldi-α-naphthyldithiourea was found to be practically insoluble in all the ordinary solvents: after washing with spirit, it formed a pure white powder melting at 224—225°, and desulphurised by lead or silver solutions.

From methylaniline, symmetrical *succinyldimethyldiphenyldithiourea* was obtained,—

$$C_2H_4[CO\cdot N{:}C(SH)\cdot NMePh]_2,$$

deposited from hot alcohol in rosettes of needles, m. p. 137—138°; resembling the preceding compound in properties, and decomposed by warm dilute potash, forming unsymmetrical phenylbenzylthiourea (Werner, *Proc. C. S.*, 1892, 96).

Succinyldiphenyldisemithiocarbazide,—

$$C_2H_4(CO\cdot NH\cdot CS\cdot NH\cdot NHPh)_2,$$

from the thiocarbimide and phenylhydrazin, occurred in crystals, melting at about 220°. With anhydrous alcohol, the thiocarbimide afforded the *dithio-diurethane*,—

$$C_2H_4(CO\cdot NH\cdot CS\cdot OEt)_2;$$

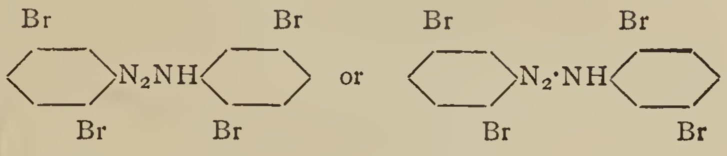
thick white prisms, insoluble in water, soluble in alcohol, desulphurised by warming with ammoniacal silver or alkaline lead solutions, and melting at 166—167°.

From phthalyl chloride and lead thiocyanate, similarly, a solution of phthalyldithiocarbimide was prepared; it appears to be a crystalline solid, but could not be obtained in a pure condition. With *water*, it yields phthalic and thiocyanic acids; and combines with bases, like the succinyl analogue, forming thioureas the examination of which is not yet complete. The *aniline* derivative melted at 209—210°; the *orthotoluidine* and *benzylamine* derivatives at 152—153° and 163° respectively. Secondary *butylamine* produced a red oil, and *methylaniline*, vitreous prisms melting at 184—185°, and decomposed by fuming nitric acid, with production of a tetranitromethylaniline, $C_6H_2(NO_2)_3\cdot NMe(NO_2)$, m. p. 127°.

69. "*The Action of Nitrous Acid on Dibromaniline*, $C_6H_3BrBr\cdot NH_2 = 1:4:2$." By Raphael Meldola, F.R.S., and Ernest R. Andrews.

During the course of some experiments on the dihaloid derivatives of β-naphthylamine which are still in progress it has been found that under certain conditions nitrous acid converts these compounds into diazoxides with the elimination of one atom of the halogen. In order to see whether this property was possessed by analogous compounds of the benzene series, paradibrombenzene was nitrated and converted by reduction into the dibromaniline, m. p. 51—52°, described by Meyer and Stüber (*Ann.*, clxv., 180). It is of interest to record that this dibromnitrobenzene cannot be reduced by zinc dust and acetic acid in alcoholic solution, in the same way that the corresponding naphthalene derivatives can be reduced to β-naphthylamine derivatives (Meldola and Desch, *Trans.*, 1892, 768). In order to effect complete reduction, it is necessary to boil the alcoholic solution with tin and hydrochloric acid in the usual manner.

The conditions favourable for the formation of diazoxides in the naphthalene series, are that the diazotising operations should be carried out in presence of an excess of strong sulphuric acid and that the diazo-salt should be warmed with dilute sulphuric acid to complete the transformation. If these conditions are not complied with the diazoamido-compound is formed instead of the diazoxide. In the present case, therefore, the dibromaniline was dissolved in glacial acetic acid, an excess of strong sulphuric acid poured in, and a little more than the calculated quantity of sodium nitrite added in small portions with constant stirring; the solution was kept cooled during this operation. When all the nitrite had dissolved, the solution was very gradually diluted with water; a clear liquid was obtained, and at this stage the solution no doubt contains the diazo-sulphate. On warming the solution for some hours nitrogen was evolved, and a brown substance separated out. The latter was not soluble to any extent in boiling water and did not therefore appear to contain a diazoxide; it was not dissolved in appreciable quantity by dilute alkali, and did not therefore contain anything phenolic. After many crystallisations from benzene, the compound was obtained in the form of brownish flattened needles melting at 234—235°. Analysis proved that it was the diazoamido-compound and that the formula was—



0·0838 gave 5·85 c.c. moist nitrogen at 12° and 752·3 m.m. N = 8·19.
0·0975 gave 0·1431 AgBr. Br = 62·46.

The formula requires N = 8·19 and Br = 62·38 per cent.

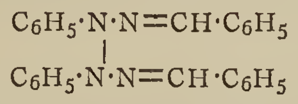
An attempt to transform this diazoimide into an amidoazo-compound was not successful; it decomposes very readily, forming dibromaniline, when treated with aniline and aniline hydrochloride in the usual way. The chief point of interest in the present note is the fact that dibromaniline so readily forms a diazoamido-compound in presence of an excess of sulphuric acid. Analogous experiments without this excess of acid have led to similar results with the corresponding dichloraniline, but these are not so remarkable under the conditions specified (Zettel, *Ber.*, 1893, 2471; and Herschmann, *Ber.*, 1894, 767).

Tribromaniline, $C_6H_2\cdot NH_2\cdot Br\cdot Br\cdot Br = 1:2:4:6$, also fails to give a diazoxide when diazotised in the presence of excess of sulphuric acid.

70. "*A New Modification of Benzilosazone.*" By Harry Ingle, Ph.D., B.Sc., and Harold H. Mann, B.Sc.

By the action of iodine on a mixture of benzalphenylhydrazone and sodium ethylate suspended in ether, the authors obtained two substances. On treatment of the mixture with ether or ethyl acetate, it was separated into its components.

The insoluble portion on re-crystallising from benzene was obtained in difficultly soluble, silky, yellow needles, melting at 186° C., identical with dibenzaldiphenylhydrotetrazone already described by Minunni (*Gaz. Chim. Ital.*, xxii., 2, 217), and by v. Pechmann (*Ber.*, xxvi., 1045), to which the formula—

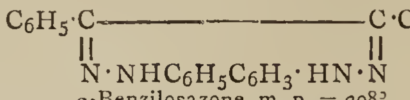


$$\begin{array}{c} C_6H_5\cdot N\cdot N{=}CH\cdot C_6H_5 \\ | \\ C_6H_5\cdot N\cdot N{=}CH\cdot C_6H_5 \end{array}$$

has been assigned.

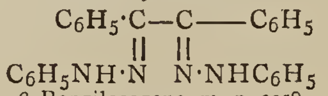
On evaporating off part of the solvent and adding alcohol to the residue, the soluble portion separated as a yellow crystalline powder. This proved to be a stereoisomeride of benzilosazone, and since it is the least stable the authors have named it α-benzilosazone.

α-Benzilosazone crystallises from a mixture of benzene and alcohol in faintly yellow-coloured prisms, melting at 208° C. On heating its solution in ethyl succinate, benzoate, or malonate to the boiling-point, or by heating it in a sealed tube with alcohol to 210° C., it is changed into the normal or β-benzilosazone (m. p. = 225). Phenylhydrazine also brings about this change. When heated on the water-bath with alcoholic potash it is unchanged, unlike the isomeric dibenzaldiphenylhydrotetrazone which is converted by this treatment into β-benzilosazone by a remarkable intramolecular transformation. If the two osazones are treated with concentrated sulphuric acid, a wine-red colour is in each case produced. On adding water to the sulphuric acid solutions and subsequently distilling in steam, the α-osazone yielded benzil, benzaldehyd, and triphenylosotriazole (Auwers and V. Meyer, *Ber.*, xxi., 2806), while from the β-osazone (m. p. = 225°) the two latter substances were not produced. These facts, by analogy with the decomposition of the stereoisomeric benzildioximes, lead the authors to assign the syn-configuration to the α- and the anti-configuration to the β-osazone.



$$\begin{array}{l} C_6H_5{\cdot}C\text{————————}C{\cdot}C_6H_5 \\ \quad \| \qquad\qquad\qquad\quad \| \\ N{\cdot}NHC_6H_5C_6H_3{\cdot}HN{\cdot}N \end{array}$$

α-Benzilosazone, m. p. = 208°.
Benzilsynosazone.



$$\begin{array}{l} \qquad C_6H_5{\cdot}C\text{—}C\text{——}C_6H_5 \\ \qquad\qquad \| \quad \| \\ C_6H_5NH{\cdot}N \quad N{\cdot}NHC_6H_5 \end{array}$$

β-Benzilosazone, m. p. 225°.
Benzilantiosazone.

This view is supported by the fact that the α-compound is the more easily oxidised. The two osazones show also different solubilities in various liquids.

The experiment of v. Pechmann (*loc. cit.*), who oxidised benzalphenylhydrazone with amyl nitrite in ethereal solution, was repeated, and from the mother-liquors the authors obtained a new substance, m. p. = 202°. Analysis showed it to be isomeric with the compounds before mentioned, but it differed from them in not being changed by alcoholic potash, or by heating with ethyl succinate; but, like the hydrotetrazone, it was reduced by phenylhydrazine to the original benzalphenylhydrazone. The constitution of this substance has not yet been determined with certainty.

71. "*Affinity of Weak Bases.*" By J. Walker, D.Sc., and E. Aston, B.Sc.

A method is described for estimating the strength of organic bases, such as aniline, from the rate at which equivalent solutions of their hydrochlorides invert cane-sugar at 60°. The results obtained are, as a rule, in agreement with those of previous experimenters. The same method applied to the nitrates of cadmium, zinc, lead, and aluminium gives the bases of these salts in the order of strength named.

72. "*Substitution-derivatives of Urea and Thiourea.*" By Augustus E. Dixon, M.D.

During the course of an investigation in which the author was engaged, it became necessary to verify the melting-points of certain urea and thiourea derivatives, and to obtain data regarding a number of compounds, hitherto unknown, belonging to the above classes. The following substances are described:—

Trimethylthiourea.—Thick, pointed prisms, very freely soluble in water, alcohol, and chloroform; desulphurised by silver, but not by alkaline lead solution, and melting at 87—88°.

Tribenzylthiourea forms silvery prisms, m. p. 114·5—115·5; insoluble in water, difficultly soluble in alcohol, freely in chloroform and benzene; decomposed on distillation.

Phenylmetatolylthiocarbamide, PhNH·CS·NHTo. — Vitreous prisms, insoluble in water, soluble in alcohol, ether, acetone, &c., and melting at 91—92°.

Orthoparaditolylthiocarbamide, $CS(NHTo)_2$. — Hard prisms, m. p. 172—173°, apparently undecomposed.

Phenylmetaxylylthiocarbamide.—White needles, melting at 125·5—126°; almost insoluble in water, sparingly soluble in cold alcohol, freely in chloroform.

Paratolyldibenzylthiourea, $ToN{:}C(SH){\cdot}NBz_2$. — Short thick prisms or long slender needles (from alcohol) m. p. 145—146°; desulphurised by ammoniacal silver nitrate only on boiling, and not at all by alkaline lead solution.

Isobutylurea, spermaceti-like needles, becoming strongly electrical on friction; m. p. 140·5—141·5°; freely soluble in water and alcohol.

sec.-Butylurea.—Large flattened prisms, freely soluble in water, alcohol, and hot acetone; m. p. 169—170°.

Diisobutylurea, $CO(NH\textit{i}\text{-}Bu)_2$.—Prepared from the corresponding thiocarbamide and silver nitrate; it occurred in white needles, m. p. 135—136°.

Di-sec.-butylurea, $CO(NH\textit{s}\text{-}Bu)_2$, from sec.-butylurethane and sec.-butylamine; pearly flattened needles, melting at 137—138°.

ab-Methylphenylurea, MeNH·CO·NHPh.—Broad white prisms, moderately soluble in hot water, and melting at 150·5° and 151·5°, undecomposed.

ab-sec.-Butylphenylurea. — Large prisms (from hot alcohol); m. p. 155·5—156·5° without decomposition, insoluble in hot water.

ab-Phenylmetatolylurea and *ab-Phenylparatolylurea.*—White needles, melting at 173—174° and 212—213° respectively.

ab-Orthoparaditolylurea.—Flexible needles, melting at 263—264°.

ab-Ethylbenzylurea.—Long silky prisms, becoming very electrical on rubbing; m. p. 104—105°.

ab-Benzylorthotolylurea.—Small vitreous prisms (from alcohol); m. p. 188—188·5°; insoluble in water.

ab-Benzylmetatolylurea.—Flexible silvery needles, insoluble in water, freely soluble in hot spirit, and melting at 158·5—159°.

Methylphenylbenzylurea, MeNH·CO·NPhBz. — From the corresponding thiourea and silver nitrate, occurs in pearly white crystals of m. p. 107·5—108·5°, insoluble in water, very freely soluble in alcohol, ether, and chloroform.

ab-Allylphenylurea was found to melt at 114·5—115·5°, instead of 96—97°, as recorded by Maly.

The author suggests an addition to the nomenclature of thiourea-derivatives, with a view of rendering it more explicit.

73. "*Note on some Reactions of Ammonium Salts.*" By W. R. E. Hodgkinson and N. E. Bellairs, Lieut. R.A.

From the results of some experiments on metals and strong ammonia solution in presence of air (*Proc. Chem. Soc.*, 146, 9), the authors were led to examine the action of some metals on so-called ammonium salts. They chose for this purpose such salts of oxy-acids as may be melted in a comparatively dry state without appreciable decomposition.

So far they have only examined the nitrate and sulphate. These salts were dried and carefully melted, and the metal, in foil or thin sheet, introduced. The temperature in each experiment was maintained a few degrees above the melting-point of the salt.

Most of the experiments were quantitative.

Metallic copper acts immediately on the fused salts, ammonia gas and a little hydrogen being evolved. When the temperature is maintained below 160°, the residual product is a mixture of copper sulphate or nitrate with an excess of the ammonium salts; some water also escapes, and, in the case of ammonium sulphate, a small quantity of sulphite sublimes. Nickel and cobalt act in a similar manner, but more sublimate of sulphite is obtained, and the amount of hydrogen is very small. Mercury does not act so readily, but similar products are formed. The most easily managed reactions are those with silver and palladium. Silver dissolves most easily both in ammonium sulphate and nitrate; the amount of displaced ammonia is nearly equivalent to the silver dissolved as sulphate or nitrate. It is doubtful whether any hydrogen escapes. With ammonium sulphate much sulphite sublimes.

Palladium is very nearly as active as silver, and the main difference seems to be that a pallad-ammonium salt is produced, whilst the silver merely forms nitrate or sulphate.

The ammonium group seems to be displaced and broken up by metals at temperatures just below those at which the salts undergo re-solution if heated alone. In no case is the exact equivalent of ammonia to that of dissolved metal obtained. The metallic salt is always in excess, but silver dissolves more readily in fused ammonium sulphate than in sulphuric acid, probably owing to the easy fusibility of the mixed salts, silver sulphate and ammonium sulphate.

Research Fund.

A meeting of the Research Fund Committee will be held in June. Applications for grants, accompanied by full particulars, should be sent to the Secretaries before June 15th.

NOTICES OF BOOKS.

The Standard Dictionary of the English Language. London: Funk and Wagnall's Company, 44, Fleet Street. 1895.

The second and final volume of this excellent work has now come before us; the promise of the first volume is fully maintained in this, the completion.

There are many new and valuable features in this Dictionary; it has a vocabulary of more than 300,000 words, or 75,000 more than the most recent of its predecessors; in electricity alone something like 4000 new terms have been entered and described.

Its production has engaged the attention of no fewer than 237 editors and specialists, besides a staff of 500 readers, while the enormous sum of 960,000 dollars was expended before a single copy was ready for the market.

The remarks we made anent the first volume do not need repetition; it will suffice to say that the whole is a monument of industry and enterprise, and will assuredly rank as one of the best Dictionaries of the English and American languages.

At the end of this volume we find, in addition to the Dictionary proper, many useful adjuncts. There is a long list of many pages of words the spelling of which is doubtful or disputed; there is a glossary of foreign terms and quotations, with a curious list of obvious mistranslations by well-known authors; while it is also claimed that, for the first time in Dictionary-making, an attempt has been made to reduce the compounding of words to a scientific system. The new or phonetic spelling is still persisted in (to a certain extent), but we do not yet see any indication of its obtaining a firm footing, at least at this side of the Atlantic.

Chemical Laboratory Labels. Part 2, Third Edition. Compiled by W. H. Symons, F.I.C. London: Published by A. Gallenkamp and Co.

This part of the label book has been thoroughly revised and considerably extended since the previous edition, and planned, as far as possible to meet the requirements of the Science and Art Department; it now contains over 750 labels, and, in addition to the name of the substance, formulæ weights have in some instances been added. There is also a series of what may be described as special labels, *i. e.*, decinormal, centinormal, quintinormal, seminormal, &c., for standard solutions, besides several pages of blanks. The labels are all gummed, and clearly printed in bold type.

CORRESPONDENCE.

THE PREPARATION OF PHOSPHINE.

To the Editor of the Chemical News.

Sir,—The preparation of phosphine by the direct combination of hydrogen and amorphous phosphorus promised so many advantages for demonstration purposes that I repeated the experiment immediately after its publication. Like Professor McLeod, I found that on passing the gas through a wash-bottle containing water and then into the pneumatic trough, it merely fumed in contact with air. No variation in the temperature or in the rate of the current of hydrogen produced a gas spontaneously inflammable. A different result was obtained on omitting the wash-bottle and passing the gas directly into the pneumatic trough. So long as the current of hydrogen was slow only the fuming was observed, but as the rate of the current was increased flashes of light appeared amidst the fumes, and, finally, when the current of hydrogen had become fairly rapid, the gas became spontaneously inflammable.

Since reading Professor McLeod's letter to you, I have repeated the experiment, and have found that by passing the gas through a glass spiral kept cool by water the same effect is obtained as when the gas is passed through a wash-bottle containing water.—I am, &c.,

George Young.

Firth College, Sheffield.
May 27, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 20, May 20, 1895.

New Researches on the Thermic Relations among the Aldehyds, the Alcohols, and the Acids.—Prof. Berthelot and M. Rivals.—The authors have undertaken further experiments, multiplying the data by their extension to the salicylic, pyromucic, and camphenic series. From the table drawn up they conclude that the change of an aldehyd, properly so-called, into an alcohol by the fixation of H_2 evolves from 13 to 17 cal. in the fatty series, for the polyatomic alcohols studied as well as for the monoatomic alcohols. From this point of view camphor belongs to the fatty series. But we know that camphor by its easy conversion into cymene furnishes the connecting link between this series and the benzenic series. The change of an aldehyd into an acid by fixation of O liberates 60 to 68 cal., except for campholic aldehyd, which belongs to a group possessing special characters and yields only +48·8. If we consider the oxidation with reference to the alcohols in its two successive degrees, formation of aldehyds and formation of acids, we find that the first degree liberates in general less heat than the second.

Existence of Phosphorus in Oysters in a Notable Proportion.—A. Chatin and A. Müntz.—The authors, in their recent analyses of oysters, have found an unexpected proportion of calcium phosphate, and have observed that this proportion is much greater in the Portuguese oyster (*Gryphæa angulata*) than the French oyster (*Ostrea edulis*). The shells of the Portuguese oyster contain 0·089 per cent, whilst those of the French oyster contain only 0·038. The same superiority was observed in the former when the two kinds had been raised for a year in the same beds at Sable-d'Olonne. The flesh in 100 parts of dry organic matter yielded, in the French species, 1·836 of phosphoric acid, and in that of Portugal 2·052.

Classification of the Chemical Elements.—Lecoq de Boisbaudran.—(See p. 271).

Spectral Analysis of the Gases given off by various Minerals.—Prof. Norman Lockyer.—On heating minerals *in vacuo* and examining the gas obtained by this process I have already found about 60 spectral lines which are, I believe, new in terrestrial chemistry. Among these minerals was uraninite, from which Prof. Ramsay has obtained a gas showing in the yellow the line which in 1869 I referred to the hypothetical element helium. Hitherto I have examined 18 minerals. The spectra show that several gases are here in question. The author gives tables of the approximate λ of the lines already photographed and remarkable coincidences of these wavelengths with those of the unknown lines in the white stars of Orion and in the chromosphere of the sun.

Hydrogenising Properties of the Sodium Alcoholates at High Temperatures.—A. Haller and J. Minguin.—The authors have extended the study of this action to various bodies having a ketonic function, especially to desoxybenzoine, benzophenone, and anthraquinone.

Comparison between the Spectra of the Gas of Clèveite and that of the Solar Atmosphere.—H. Deslandres.—This memoir will be inserted in full.

Isomeric Transformations of the Salts of Mercury.—Raoul Varet.—A table of the heat disengaged on the reciprocal metamorphoses of the salts of mercury in their isomeric states.

Action of Nitrogen Peroxide on the Haloid Salts of Antimony.—V. Thomas. — Not suitable for useful abstraction.

Formation Heats of Benzoyl and Toluyl Chlorides.—Paul Rivals.—The formation heat of liquid benzene (−4·1 cal.) and of solid benzoic acid (+94·2 cal.) gives a difference of +98·3 cal.

A Study of Senecionine and Senecine.—A. Grandval and H. Lajoux.—The authors have operated upon *Senecio vulgaris.* Senecionine has the composition $C_{18}H_{26}NO_6$. It does not display striking reactions. Senecine is incomparably more bitter than senecionine. Its analysis is not given. With sulphuric acid it gives a yellowish colouration, inclining to brown; with nitric acid a reddish violet colour and a deep violet precipitate. With sulpho-vanadic acid a violet-brown colour.

On Benzene-sulpho-orthotoluidine and some of its Deeivatives.—Ch. Rabaut.—The author points out the great resistance of benzene-sulpho-orthotoluidine to oxidation, and its great stability in presence of hot dilute acids, notwithstanding its character as an amide.

Analysis of the Bones of a Mummy.—M. Thezard'—The tibia of an adult, white, very brittle, and of uncertain date. Some of the tombs from which it has been procured date back to 4500 B.C., and others only to 665 to 527 B.C., or even to the epoch of the Ptolemies, 306—30 B.C. Its composition is:—

Moisture	7·900
Organic matters (nitrogenous)	19·769
Fatty matter	0·850
Other organic matter	3·412
Tricalcic phosphate	50·940
Magnesium phosphate ($2MgO,PO_5$)	2·095
Calcium carbonate	10·365
Potassium nitrate	0·270
Sodium nitrate	0·644
Sodium chloride	1·338
Sodium sulphate	0·469
Iron oxide	0·240
Alumina	0·534
Silica	0·800
Fluorine	traces
Not determined	0·374
	100·000

On a Leucomaine obtained from the Urine of a Patient suffering from Angina pectoris.—Dr. A. B. Griffiths and C. Massey.—This base is white and crystalline, soluble in water; reaction slightly alkaline. It forms a crystalline hydrochlorate, chloroplatinate, and chloraurate. It gives a yellowish precipitate with phosphotungstic acid, a yellow with phosphomolybdic acid, a red with tannic acid, and a greenish with silver nitrate. With mercuric chloride it gives a green precipitate, and with Nessler's reagent a brown precipitate. Its composition agrees with the formula $C_{16}H_9NO_4$. It is very poisonous, producing fever and death in two hours. It is not present in normal urine.

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Tests for Morphine in Urea.—(Reply to A. R. P.).—An article on the "Recovery of Absorbed Morphine from the Urine, the Blood, and the Tissues," by Dr. T. G. Wormley, appeared in the Chemical News for August 8, 1890 vol. lxii., p. 65).—T. G. W.

Deodorising Petroleum.—Will some correspondent kindly inform me if there is an inexpensive way of removing the odour from petroleum oil. I want to mix it with another substance, but the smell the oil imparts would make it most disagreeable.—C. R.

MEETINGS FOR THE WEEK.

Tuesday, 11th.—Medical and Chirurgical, 8.30.
—— Photographic, 8.
Thursday, 13th.—Royal, 4 30.
—— Royal Society Club, 6.30.
—— Mathematical, 8.
Friday, 14th.—Physical, 5. "The Measurement of Cyclically varying Temperature," by H. F. Burs'all. "The Thermal Constants of the Elements," by N. F. Deere, "An Electromagnetic Effect," by F. W. Bowden.
—— Astronomical, 8.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1855.

ON THE DENSITY OF HELIUM.*

By M. CLÈVE.

M. Langlet, who is occupied in the University of Upsala on the study of helium, has lately determined its density. The gas extracted from clèveite was freed from hydrogen by passing it over oxide of copper heated to redness, and from nitrogen by means of metallic magnesium. It did not contain argon. Its density was found to be 0·139 (air = 1), or 2·02 (hydrogen = 1). This number is decidedly lower than the density found by Professor Ramsay. We are now occupied in determining the specific heat of the gas.

[Some weeks ago Professor Ramsay told me that he had obtained helium, pumped off at a red heat from brüggerite, of as low a density as 2·18.—*Ed. C. N.*]

SOLAR AND TERRESTRIAL HELIUM.

The Editor has the writer's permission to print the following private letter to himself:—

Runge having stated (*Nature*, June 6, 1895, p. 188) that the yellow line of the gas which he obtained from clèveite is double, and that neither of the component lines has exactly the place of the helium line, which falls between them, this new gas, as Runge points out, cannot be helium, unless the bright line D_3 in the sun is similarly double.

Though I had no doubt from former observations of my own, as well as from the measures of the line by Jewell for the Rowland tables, that the solar line is single, I have now examined the line again with a 4-inch Rowland grating of 14,438 to the inch, using the third order of spectrum, and a magnifying power of 29 diameters.

At the sun's limb the helium line appeared, as it usually does of some breadth, but at favourable moments I saw the line, as also did Mrs. Huggins, fine off to a very fine single point.

There can be no doubt that the helium line in the sun is not double, as Runge states the new gas line to be.

In this connection I may mention observations of Bélopolskŷ (*Mem. Società Spett. Ital.*, May, 1894), who saw occasionally a pair of dark terrestrial lines come in at the sides of the bright helium line.

The wave-lengths of these lines agree pretty well with Runge's measures. May it be that the clèveite gas is the stuff giving rise to these terrestrial lines? A similar suggestion was made to me some weeks ago by Dr. Blumbach, before Runge had shown the new gas line to be double.

Bélopolsky's measures are given in the Potsdam scale, which differs from that of Rowland by less than one unit in the first decimal place.

Runge's measures.	Bélopolsky's measures.
5875·883	5875·8
(Helium.. 5875·982)	(Helium.. 5876·0)
5876·206	5876·5 (double)

The measures for D_1 and D_2 are—

Potsdam.	Rowland.
5896·25	5896·156
5890·23	5890·188

William Huggins.

90, Upper Tulse Hill, S.W.,
June 10, 1895.

TERRESTRIAL HELIUM (?).

By Professor C. RUNGE.

The following communication appeared in last week's *Nature*:—

Prof. Paschen and I have lately made a careful determination of the wave-length of the strong yellow line emitted by clèveite when heated in a Plücker tube. We owe the mineral to the kindness of Prof. Rinne. My large Rowland concave grating, of 6·5 metre radius, clearly shows the yellow line to be double. Its less refrangible component is much weaker, but comes out quite bright when the stronger one is brilliant. We photographed the two lines together with the second order of the spark spectrum of iron. There are a number of iron lines on each side that are included in Rowland's list of standard wave-lengths (*Phil. Mag.*, July, 1893). From these we interpolated the wave-lenths of the yellow lines by micrometric measurement. Three different plates taken on different days gave us—

Strong component.		Weak component.
5875·894	.. .. ..	5876·216
5875·874	.. .. ..	5876·206
5875·880	.. .. ..	5876·196
Mean 5875·883		Mean 5876·206

We think an error of more than 0·025 very improbable.

Now Rowland's determination of D_3 (*Phil. Mag.*, July, 1893) is—

5875·982,

the result of three series of measurements which he believes to be accurate to 0·02.

The difference between this value and the wave-length of the strong component is much too large to be accounted for by an error of observation.

We do not therefore agree with the conclusion, drawn by Mr. Crookes, that the unknown element helium causing the line D_3 to appear in the solar spectrum is identical with the gas in clèveite, *unless D_3 is shown to be double.* Perhaps Prof. Rowland will tell us if this might have escaped his notice. From his note on D_3 in *Phil. Mag.*, July, 1893, it appears that D_3 cannot have been so wide as to include both lines, because he would then not have considered his determination accurate to 0·02. As for dispersion, one may see in his table of solar spectrum wave-lengths that he has frequently measured three and even four lines in an interval as large as the one between the components.

Hanover Techn. Hochschule, May 16.

CERIUM,

By BOHUSLAV BRAUNER, Ph.D., F.C.S.,
Late Berkeley Fellow of Owens College.

During the last seventeen years I have been engaged in the investigation of the rare earth-metals of the cerium group, and the results obtained by me were published in the years 1881, 1882, 1883, 1885, 1888, and 1891, in the *Journal of the Chemical Society*, in the *Proceedings* and the *Transactions of the Vienna Academy*, the *Comptes Rendus*, and the *Berichte*.

One of the papers was devoted to the study of the atomic weight of cerium. It was shown in that paper most distinctly that ordinary cerium is a mixture of two substances, the real cerium with the atomic weight of 140·2 giving a nearly white oxide, and a substance giving an oxide of a peculiar *flesh-colour mixed with orange*, with a higher atomic weight. The last was found to rise to 142·65, and even to 145·72. Fractions showing this high atomic weight were obtained on precipitating the mother-liquors, from which the sulphate of the ordinary

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* A letter from M. Clève to M. Berthelot, in the *Comptes Rendus* for June 4th, 1895 (vol. cxx., p. 1212).

cerium has crystallised out, by alcohol. Knowing the difficulty of my position, I was too modest to declare the substance as the compound of a new element, and only concluded that "under certain conditions 'cerium' may consist of a mixture, The nature of this admixture must be ascertained by further experiments."

Schützenberger has lately (*Comptes Rendus*, cxx., 633 and 962, and Chemical News, lxxi, p. 188) published two papers on the same subject. He obtained cerium by Debray's method, and it was split up exactly by the same method which was used and described by me ten years ago into "cerium (1)," with a nearly white oxide and the atomic weight 139·5, and "cerium (2)," with an oxide "rouge rosé ou brun rose clair." The synthesis of the sulphate gives numbers varying between 142·4 and 143·3.

I am very sorry to remark that not the slightest reference was made here to my work, though the method used and many of the results obtained by the illustrious French chemist are absolutely the same as those described by me in English and German.

The novelty of Schützenberger's research consists in using Debray's method, and in establishing the fact that other methods of analysis give for the atomic weight of "cerium (2)" results varying between 136 and 138·75.

In order not to lose the priority of the above discovery and the right of continuing my research, I may be allowed to give a short account of the results obtained by me during the last years.

I devoted first my attention to the study of the salt, which was considered formerly as a sulphate of the trioxide Ce_2O_3 as long as cerium was regarded as divalent $Ce=94$. (With $Ce=141$ this oxide becomes Ce_4O_9.) The old formula was—

$$2CeSO_4.Ce_2(SO_4)_3+18H_2O.$$

Mendeleeff in 1873, on proposing the new atomic weight of cerium (*Ann.*, clxviii., p. 45), regarded the salt as a double sulphate of trivalent cerium with tetravalent cerium:—$Ce_2O_3.3SO_3+Ce_2O_4.4SO_3+24H_2O$.

I have proved by the following methods that the salt possesses really the composition assumed by Mendeleeff:—

1. By numerous analyses of the salt. By this method alone, unfortunately, no constant results could be obtained, for the salt, crystallising only from a solution which contains much free sulphuric acid (*i.e.*, 25 per cent H_2SO_4!), always contains a considerable excess of this acid, probably mechanically included.

2. By synthesis of the salt from the single constituents, $Ce_2(SO_4)_3.8H_2O$ and $Ce_2(SO_4)_4.8H_2O$.

3. Trivalent cerium was replaced by other trivalent earth-metals and their sulphates, combined with the tetrad ceric sulphate. In this way a *new series of double sulphates* of trioxides with those of cerium tetroxide was obtained, and, as they show a great similarity of form with Mendeleeff's salt, they are being crystallographically investigated by Prof. Urba. The new lanthano-ceric salt is an example, and its analysis agrees, though not quite well, with the formula—

$$La_2O_3.3SO_3+Ce_2O_4.4SO_3+24H_2O.$$

4. The synthesis and analysis of the salt *alone* not proving sufficient for the establishment of the formula, the mother-liquors from which the salt has separated were analysed completely, and found to contain 26·18 per cent of sulphuric acid, only partly combined to cerium and lanthanum. The molecular proportion of its constituents is, in round numbers, $1R_4O_7 : 23SO_3 : 333H_2O$, and it is easily understood that, by an inclusion of such a highly acid mother-liquor, the composition of the salt is most considerably altered. After applying a correction for the included mother-liquor, the formula of the above salt becomes $La_2O_3.3SO_3+Ce_2O_4.4SO_3+18H_2O$.

This salt throws some light on the real composition of the analogous ceroso-ceric sulphate which was at first regarded by me as an acid salt. But this view was given up, as the salt rarely contains so much free sulphuric as to correspond with the composition of an *acid sulphate*.

Some work was devoted also to the preparation of the tetrachloride of cerium and its double salts, corresponding with the tetrafluoride and its double salts discovered by me (1882); the result was obtained that ceric hydrate exists in two modifications. The one is insoluble in cold hydrochloric acid, the other dissolves in hydrochloric acid; but the brownish-yellow solution of the tetrachloride obtained decomposes even at the temperature of −18° with evolution of chlorine.

I have devoted much time to attempts to split up cerium into its constituents, and succeeded in doing so, more or less completely, by the following experiments:—

1. By fractional solution of ceric oxide in sulphuric acid. The remaining portions were absolutely insoluble in boiling concentrated sulphuric acid, and after being brought into solution either by fusion with $KHSO_4$ or by boiling with hydrochloric acid and potassium iodide, the oxalate gave on ignition a rose-brown (dark salmon-coloured) oxide of an element, which I would design provisionally as "meta-cerium."
2. By partial reduction of ceric oxide in hydrogen, and extraction of the products obtained.
3. By fractional precipitation with oxalic acid.
4. By fractional crystallisation of the sulphate, and precipitation of the mother-liquor by alcohol. (This method was used and described by me ten years ago.)
5. By fractional crystallisation of the *ceric*-ammonium nitrate.
6. By fractional crystallisation of the *cerous*-ammonium nitrate. (This is Mendeleeff's method, *l.c.*, and was accepted by Auer von Welsbach without reference to Mendeleeff.)
7. The new earth is accumulated in the mother-liquor after precipitation of cerium as basic nitrate or sulphate, and can be obtained from them by combining Debray's method with one of the above methods.

I have also examined the spark spectra of the different fractions of cerium, and I find that some lines are common to cerium and to meta-cerium, whereas other lines are characteristic for each of them.

Not being satisfied with the results of my former method of atomic weight determination of cerium, by the conversion of the anydrous cerous sulphate into ceric oxide, the results of which varied between 140·03 and 140·43, on account of the slightly varying composition of ceric oxide, I made a new series of determinations based on the analysis of the normal *oxalate* by the method of Gibbs (*Proc. Amer. Acad.*, xxviii., 260—279). In order to exclude the error due to the varying composition of the ceric oxide, the quantity of "active" oxygen contained in it over and above Ce_2O_3 was most carefully determined by Bunsen's method (*Ann.*, cv., 40), and care was taken to introduce a correction due to the liberation of a trace of iodine during the action of 10 c.c. hydrochloric acid upon 1 gr. KI, as found by a blank experiment.

The determinations may be checked by determining the amount of water contained in the air-dry oxalate and the oxalate dried over phosphorus pentoxide, and by the synthesis of the sulphate from the oxalate.

The determination of the oxalic acid radical was done by *old* potassium permanganate of an invariable standard. This last mode of determination requires great practice, because, as soon as all oxalic acid is oxidised, the trivalent cerium present begins to be oxidised to the tetravalent state, but not sooner, as oxalic acid is oxidised by ceric sulphate, a reaction which can be used for the volumetric determination of ceric salts. The details of one of the determinations show the applicabilty of the method:—

100 parts of the pure cerous oxalate were found to contain (*a*) 29·506 p.c. C_2O_3, (*b*) 29·503 p.c. C_2O_3, and (*c*) 46·934 p.c. of the dioxide. This contains surplus oxygen, (*d*) 2·155 p.c. (corrected), and (*e*) 2·235 p.c. (uncorrected). The atomic weight of cerium, calculated from (*a*), (*b*), and (*c*), is $Ce=139·91$; that from (*a*), (*b*), (*c*), and (*d*), $Ce=140·01$;

from (*a*), (*b*), (*c*), and (*e*), $\mathrm{Ce}=139{\cdot}72$. The third number shows that a correction of the above kind must be introduced; the first and the second methods of calculation give numbers differing only slightly from each other, and the method of analysis is entirely free from the great variations inherent to the methods used by Schützenberger. It has been shown by many chemists, and especially by Th. W. Richards in his wonderfully exact researches, that the method of determining sulphuric acid as barium sulphate (not to say in the presence of alkalies, as done by Schützenberger!) is so vicious as to prove *absolutely inapplicable* for the determination of atomic weights, and very little confidence can therefore be placed in the number $\mathrm{Ce}=139{\cdot}5$, found by this method by Schützenberger.

I prefer the number $\mathrm{Ce}=140{\cdot}01$ obtained by me by the above combined method, after applying the said correction, and regard it as an exact determination of the atomic weight of cerium.

The fact that potassium permanganate oxidises colourless *cerous* salts to yellow *ceric* salt was used by me for the volumetric determination of cerium. In an acid solution the end of the reaction cannot be seen, on account of the deep yellow colour of the ceric salt formed. The method gives, however, excellent results in alkaline solution:—

$$3Ce_2O_3+2KMnO_4+H_2O+Aq= \\ =2KOH+2MnO_2+3Ce_2O_4+Aq.$$

The excess of permanganate used is determined in the filtrate, after removal of the hydrated oxides formed by filtration through a Gooch.* This method has proved invaluable for the determination of trivalent cerium in the presence of tetravalent cerium, and of cerium in any form (tetravalent cerium may be first reduced by sulphurous acid) in the presence of other non-oxidisable earths. The results obtained for the "atomic numbers" of "meta-cerium" give invariably higher numbers in contradistinction to the results obtained by Schützenberger.

I think that these higher numbers are correct also for the theoretical reason that there is no room in the periodic system for a cerium-like element with a lower atomic weight than cerium. On the other hand, many rare earth-metals may exist with higher atomic weights than 140. The most interesting question—whether "meta-cerium" is not Mendeleeff's "ekacerium" of 180?—will have to be answered by further investigation.

Before concluding this preliminary notice some theoretical remarks may be allowed. The question arises—Where is there a place in the periodic system for the numberless rare earth-metals (true chemical asteroïds) the atomic weight of which varies between 140 and 170? The following suggestion may throw some light on that question:—

On considering the position of the rare-earth elements in the periodic system, we arrive at the following conclusion:—"*The valency of the rare-earth elements increases with increasing atomic weight.*"

Beryllium, $\mathrm{Be}=9$, is undoubtedly a *divalent* rare-earth element, with the oxide RO, as was shown by the author in 1878, 1881, and 1882.

Then come the *trivalent* elements: scandium, $\mathrm{Sc}=44$; yttrium, $\mathrm{Y}=89$; lanthanum, $\mathrm{La}=138$; and ytterbium, $\mathrm{Yb}=173$, with the oxides, R_2O_3.

Cerium, $\mathrm{Ce}=140$, forms a transition to the tetravalent earth elements, being both *trivalent* and *tetravalent*, with the oxides R_2O_3 and R_2O_4.

Thorium, $\mathrm{Th}=232$, is only *tetravalent* with the oxide R_2O_4, though a lower oxide, Th_2O_3, may exist, corresponding to the lower oxides of niobium and tantalum.

At the present limit of the periodic system and outside it rare-earth elements may be expected, possessing the oxides R_2O_5, R_2O_6, and perhaps even R_2O_7 and R_2O_8, with distinct basic properties. Very probably the atomic weight of either neodymium ($R'''=140{\cdot}5$) or praseodymium ($R'''=143{\cdot}5$) will be 235 and the oxide R_2O_5, or 282 and the oxide R_2O_6 (a true Neptune of the periodic system), for only one of both constituents of the old didymium, more probably praseodymium, yielding salts of the higher oxide, which seems to be as unstable as is $CeCl_4$ (see above), will find its place in the eighth series next to cerium.

The association of the rare-earth minerals with argon and helium, and their rarity on the surface of the earth, indicate that we have to do here with the heaviest atoms, the normal geological position of which is in the interior of our earth.

Being obliged to do all this and other difficult work myself alone, without the slightest assistance or help, my time does not allow me to go on so quickly with my work as I would like it; and had it not been for the fact that Schützenberger has repeated a great part of my work without making any reference to it, I should have delayed the publication of the results arrived at years ago until the character of the new constituent of cerium could have been described more definitely.

Bohemian University, Prague,
May 28, 1895.

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[*] This method may be used for the determination of a large number of elements giving lower and higher oxides.

NOTE ON THE ESTIMATION OF TOTAL ALKALI IN SOAP.

By J. A. WILSON.

In titrating soap solutions by standard acid, especially in the case of soap prepared from solid fats, as tallow, palm oil, &c., the end of the neutralisation when using methyl orange as indicator, at a temperature of, say, 25° C., is not very definite, the pinkish tint gradually disappearing on violent stirring. This is due to traces of the soap solution becoming enveloped in the precipitated fatty acids, and then not easily being acted upon by the acid employed in titration.

The error is great enough to render determination of the free alkali (by difference) unreliable, and I have now given up direct titration.

The following examples illustrate the above remarks:—

	Percentage of Na_2O.	
Sample No.	Direct.	Indirect.
63.	6·71	6·94
35.	5·43	5·54
98.	8·28	8·39

Newchurch, Rossendale,
May 27, 1895.

MELTING-POINT OF THE ELEMENTS AS A CLUE TO THEIR GENESIS.

By C. T. BLANSHARD, M.A.

A. Baeyer was the first to observe (*Ber.*, x., 1286) that in several series of organic compounds the melting-points are alternately high and low with each increment of the grouping CH_2. He further observed that compounds containing an even number of carbon atoms have high melting-points, whilst those with an uneven number have comparatively low melting-points. Thus, to take as an example the fatty acids, as, all being tolerably well known bodies, these afford plenty of data, we have the following figures from the most recent sources. I quote from H. Landolt and R. Börnstein, "Physikalische-Chemische Tabellen," Berlin, 1894.

Compounds.		Formula.	High m.p. °	Low m.p. °
Formic acid	.. ..	CH_2O_2		8·6
Acetic acid ..	.. ..	$C_2H_4O_2$	16·75	
Propionic acid	.. ..	$C_3H_6O_2$		−24
Butyric acid	.. ..	$C_4H_8O_2$	−4	
Valeric acid	.. ..	$C_5H_{10}O_2$		below −16
Caproic acid	.. ..	$C_6H_{12}O_2$	−1·5	
Œnanthylic acid	..	$C_7H_{14}O_2$		−10·5
Caprylic acid	.. ..	$C_8H_{16}O_2$	16·5	
Pelargonic acid ..	..	$C_9H_{18}O_2$		12·5
Capric acid ..	.. ..	$C_{10}H_{20}O_2$	29·5	

The acids considered are the normal ones.

If the elements are arranged in their natural groups, and the melting-points compared, no such alternation is found. But an arrangement of the elements in order of atomic weight, that is to say in periodic series, reveals such alternations of high and low melting-points. The melting-points given are those to be found in an article in the January number of the *Phil. Mag.* for this year ([5], xxxix., p. 106), with the substitution of the latest values for Cu, Ag, Mg, Zn, Al, Sb, namely those of C. T. Heycock and F. H. Neville (*C. J.*, 387, p. 186, Feb., 1895), and the addition of Olszewski's value for N. The figures here are given in round numbers. In the article in the *Phil. Mag.* referred to, the exact figures together with the authorities will be found; but it will suffice here to give fewer, and those in simpler form.

I have suggested the melting-points −200° for O, and −182° for F, for the following reasons.

Prof. Dewar (Chem. News (lxxi., p. 199) finds that air remains a half solidified jelly at −210°. Now nitrogen solidifies at −214°; it would therefore seem that the melting-point of oxygen is higher than this. The value for nitrogen is Olszewski's. With regard to fluorine the melting-point of I is 114°, that of Br 121° less than this, that of Cl 95° less than that of Br. We should therefore expect the melting-point of F to be 80° (the geometric mean) less than of Cl, viz., −182°. The other queried values have all been ascertained by able authorities, but not in definite figures.

Series 1.

Element.		°M.p.
Li	.. ..	180
Be	.. ..	900
B	.. ..	2700 ?
C	.. ..	3000 ?
N	.. ..	−214
O	.. ..	−200 ?
F	.. ..	−182 ?

Series 2.

Element.		°M.p.
Na	.. ..	96
Mg	.. ..	633
Al	.. ..	654
Si	.. ..	1200 ?
P	.. ..	44
S	.. ..	114
Cl	.. ..	−102

Series 3.

Element.		°M.p.
K	.. ..	62
Ca	.. ..	—
Sc	.. ..	—
Ti	.. ..	2500 ?
V	.. ..	—
Cr	.. ..	2200 ?
Mn	.. ..	2000 ?

Series 4.

Element.		°M.p.
Cu	.. ..	1080
Zn	.. ..	419
Ga	.. ..	30
Gl	.. ..	900 ?
As	.. ..	200 ?
Se	.. ..	250
Br	.. ..	−7

Series 5.

Element.		°M.p.
Rb	.. ..	38
Sr	.. ..	—
Y	.. ..	—
Zr	.. ..	—
Nb	.. ..	—
Mo	.. ..	—
*	.. ..	—

Series 6.

Element.		°M.p.
Ag	.. ..	960
Cd	.. ..	321
In	.. ..	176
Sn	.. ..	233
Sb	.. ..	629
Te	.. ..	455
I	.. ..	114

Series 5 and the series above the 6th do not yield any comparable results, the melting-points being very defective. Series 1 shows no alternation, but Series 2, beginning with the third member Al, probably Series 3, Series 4, beginning with the second member Zn, and Series 6, beginning with the second member Cd, all show alternation of high and low melting-points, the only exception being Sb.

The above data may be considered to establish the two following laws:—

1. With elements of both low atomicity and low atomic weight melting-point varies directly as atomic weight.
2. In the higher periodic series of elements the melting-points are alternately high and low, with increase of atomic weight.

That is to say, in all the elements but those which from their low atomic weights may reasonably be regarded as the very simplest, a relationship maintains which has been observed in numerous series of organic substances.

It is reasonable, therefore, to suppose that such elements with higher atomic weights are in reality substances of a higher grade than the others, in that they resemble such highly evolved bodies as carbon compounds, at any rate in respect of melting-point.

There is another way, however, in which a parallel can be drawn, and that is in respect of specific volume. This I must reserve for a future article.

THE ACTION OF HEAT UPON ETHYLENE.*

II.

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.

(Continued from p. 273).

Table III.

Temperature, 900° C. Rate of Flow, 40 c.c.

Length of tube heated.	1 inch.		6 inches.		18 inches.	
Volume of gas—						
Before heating ..	870		1050		1000	
After heating ..	790		985		980	
Analysis of Gaseous Products.						
Carbon dioxide ..	0·75		0·50		0·25	
Oxygen	0·50		0·75		0·50	
Unsaturated hydrocarbons	50·80		35·75		9·75	
Carbon monoxide	1·50		1·00		1·50	
Saturated hydrocarbs. by absorp.	11·22	} 27·67	11·25	} 41·75	10·00	} 56·50
Do. by explos.	16·45		30·50		46·50	
Hydrogen	14·50		16·65		28·00	
Nitrogen	4·28		3·60		4·00	

Calculating the percentage for the change in volume, we obtain the following figures:—

Length of tube heated.	1 inch.	6 inches.	18 inches.
Unsaturated hydrocarbons	46·12	33·53	9·55
Saturated hydrocarbons	25·12	39·16	55·37
Hydrogen	13·16	15·61	27·44

The original gas contained 96·7 per cent of ethylene, so that the percentages of unsaturated hydrocarbons decomposed are:—

Length of tube heated.	1 inch.	6 inches.	18 inches.
	50·58	63·17	87·15

On collecting these results in one table—

Percentage of Ethylene decomposed.

Length of tube heated.	1 inch.	6 inches.	18 inches.
5 c.c.	80·10	85·48	93·76
15 c.c.	70·83	79·42	90·31
40 c.c.	50·58	63·17	87·15

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* A Paper read before the Royal Society.

The first thing that strikes one is the enormous amount of decomposition which takes place in the first inch of flow through the heated tube, and the small effect which an increase in the length of the heated surface has upon the further decomposition of the unsaturated hydrocarbons.

This result might be caused by the methane and hydrogen formed during the decomposition diluting the remaining ethylene, and so rehdering the decomposition more difficult; it may also arise from secondary actions taking place amongst the primary products, and again forming ethylene, or it may be due to both these causes acting together.

In order to trace the effect of dilution, a series of experiments was made in which ethylene, diluted with hydrogen, was passed through 6 inches of the same tube as was used in the previous experiments, heated to the same temperature, and under precisely similar conditions.

The store holder of ethylene used for making the mixture contained a gas which gave on analysis—

Ethylene	97·85
Nitrogen	2·00
Oxygen	0·15

Table IV.

Influence of Dilution in Checking Decomposition of Ethylene.

Length of tube heated, 6 inches. Rate of Flow, 10 c.c. per minute. Temperature, 900° C.

Percentage of hydrogen	nil		10·0		25	
Do. of ethylene ..	98·7		90·0		75	
Volume of gas—						
Before heating..	100·0		100·0		100	
After heating ..	81·3		69·5		69	

Analysis of Products of Decomposition.

Carbon dioxide ..	1·00		0·75		0·50	
Oxygen	0·50		0·25		0·25	
*Unsaturated hydrocarbons ..	32·52		31·00		29·00	
Carbon monoxide	1·00		1·25		1·00	
Saturated hydrocarbs. by absorp.	17·75	50·25	14·50	50·75	14·50	48·45
Do. by explos.	32·50		36·25		33·95	
Hydrogen	12·62		14·25		18·50	
Nitrogen	2·11		1·75		2·30	
*Containing acetylene	1·06		0·52		0·73	

Percentage of hydrogen	50		75		95	
Do. of ethylene ..	50		25		5	
Volume of gas—						
Before heating..	100		100		100	
After heating ..	64		85		100	

Analysis of Products of Decomposition.

Carbon dioxide ..	1·25		0·50		—	
Oxygen	—		0·15		—	
*Unsaturated hydrocarbons ..	22·25		11·10		2·00	
Carbon monoxide	1·25		1·00		0·50	
Saturated hydrocarbs. by absorp.	8·50	36·00	5·50	15·80	0·75	4·85
Do. by explos.	27·50		10·30		4·10	
Hydrogen	37·15		68·45		89·15	
Nitrogen	2·10		3·00		3·50	
*Containing acetylene	0·32		0·15		trace	

On calculating these percentages for the change in volume, we obtain the following results :—

	I.	II.	III.	IV.	V.	VI.
Unsat. hydrocarbons ..	25·58	21·18	19·50	14·04	9·30	2·00
Saturated do.	40·85	35·27	33·43	23·04	13·43	4·85

The ethylene taken only contained 97·85 per cent of the hydrocarbon, hence—

	I.	II.	III.	IV.	V.	VI.
Unsat. hydrocarbs. originally present	97·85	88·02	73·35	48·90	24·45	4·89
Do. do. present after heating ..	25·58	21·18	19·50	14·04	9·30	2·00
Do. do. decomposed	72·27	66·84	53·85	34·88	15·15	2·89

and calculating this to percentage of total ethylene decomposed—

I.	II.	III.	IV.	V.	VI.
73·86	75·94	73·24	71·30	61·96	59·10

which shows that dilution has practically no effect in retarding the decomposition until 75 per cent of diluent is present, and also clearly points to its being radiant heat, and not contact with the heated sides of the tube, which is responsible for the largest proportion of the decomposition, as had contact been the active factor, dilution, by reducing the number of impacts of the hydrocarbon molecules with the heated surface, would have shown a considerable decrease in decomposition.

(To be continued.)

THE ADULTERATION ACTS.

There are several matters of more than ordinary interest touched upon by Mr. Frank L. Teed, public analyst to the parish of Camberwell, in the quarterly report which he has just presented to the Vestry. "Two rather curious cases," Mr. Teed states, "have recently been decided in connection with the Acts governing the Sale of Food and Drugs. In one a vendor was summoned for, and after much legal argument convicted of, the rare offence of selling a drug, diluted acetic acid, of greater strength than laid down in the British Pharmacopœia. This offence at first sight may not seem important, but when it is considered that medical men in prescribing medicines have to rely on the pharmacist supplying drugs as prescribed, and that if the pharmacist supplies a stronger drug serious consequences may arise, its importance becomes more apparent. The same offence is punishable under the Pharmacy Act with a penalty of £5, but I understand that the Secretary to the Pharmaceutical Society is the only man who can proceed under this Act. The other case has perhaps more important consequences, and that is a decision of the High Court that penalties under the Margarine Act, 1887, are to go to the prosecuting authority. It is a question of some importance whether former penalties inflicted under this Act are not still recoverable by the Vestry."

With respect to the inactivity of the Vestry in carrying into effect the Adulteration Acts, Mr. Teed remarks :—"I have from time to time felt it my duty to bring to your notice that fewer samples were taken in Camberwell in proportion to the population than in the rest of London taken as a whole. The Annual Report of the Local Government Board for 1893-94, the latest report out, states 'In London one sample was obtained for every 530 persons.' To bring Camberwell into line with the rest of London the number of samples must be more than doubled. I have placed these figures before you, as they have a direct bearing on the administration of the three Acts designed to suppress adulteration. While on the subject of the above Report I may mention that the action of this Vestry in testing the genuineness of milk as it arrives from the country is favourably commented upon. The importance of this branch of the crusade against adulteration can scarcely be over-estimated, as, in addition to other benefits, it not only protects the consuming public but also the honest retailer, struggling for existence in the whirl of the conflicting interests of mercantile competition. This Report also alludes to the high percentage of adulterated milk samples purchased on Sundays, and to the diluted condition of milk supplied to some public institutions. The minimum number of samples was not reached this quarter, only 17 samples as against 50 having been taken. I can only revive a former suggestion of mine, that an Inspector should be especially allotted to this work, not necessarily for his whole time, but the collection of the requisite number of samples to be his primary duty."

CONTRIBUTION TO THE HISTORY OF THE EARTHS OF CERITE.*

By P. SCHUTZENBERGER.

After the elimination of the cerium by melting the nitrates between 320° and 330° along with 8 to 10 parts of saltpetre, the saline mass separated from CeO_2 by solution in water, filtration, and evaporation to dryness, is fused again, and kept between 350° and 360° up to tranquil fusion. Nitrous gas is no longer evolved, except in very small quantity.

The object of this operation is the removal of the last traces of cerium. We dissolve, filter, and evaporate to dryness in order to proceed with the residue to fractionated separations by heating to higher temperatures.

Five successive fractions have thus been obtained between 400° and 420°, and three others between 430° and 460°.

The subnitrates, insoluble in water, separated each time, have been converted into oxalates, and then into oxides very free from alkali.

The oxides were then heated to bright redness, and for each fraction the atomic weight was determined by converting it into sulphate. As a control we returned to oxide by igniting the anhydrous sulphate at bright redness. These operations do not present the same difficulties as those with cerium, the oxides being always brought back by ignition to the lesser degree of oxidation, M_2O_3.

The method followed is an extension of the Debray process to the separation of lanthanum and didymium.

Making use of the names generally accepted, we shall call—

1. *Earths of the ceric group;* all the earths which form double potassium sulphates, insoluble in a saturated solution of potassium sulphate.
2. *Cerium oxides:* those of the above earths which are capable of being converted into bioxides CeO_2, the colourless salts of which furnish no absorption bands.
3. *Oxides of didymium;* those of the earths which yield salts more or less rose-coloured, the solutions of which present the absorption bands of the salts of didymium, and whose ignited oxides answer to the formula $D_{12}O_3$.
4. *Oxides of lanthanum;* those of the earths whose salts are colourless without absorption rays, which when ignited answer to the type La_2O_3, and whose nitrates deliquesce in contact with moist air.

The following Table sums up the results obtained:—

	Numbers of fractionation (Series I.)	Atomic weights corresponding.
Between 400° and 420°	1	140·3
	2	140·6
	3	140·6
	4	140·6
	5	140·0
Between 430° and 460°	6	135·0
	7	138·0
	8	138·0
Nitrate not decomposed	9	138·0

During these fractionated fusions the didymium first separates, the melted and dissolved mass loses more and more its rose-colour, and after the separation of No. 8 it is colourless; No. 9 then represents lanthanum free from didymium. Thus by a single fractionation we obtain lanthanum exempt from didymium.

The oxalates of the fractions Nos. 1 to 5 yield, on limited ignition in air, an oxide of a brown colour, becoming greyish on ignition to bright redness.

The oxalates of the fractions Nos. 6 to 8 give, on limited ignition in air, a very pale brown oxide, becoming greyish-white at a bright red heat.

The fractions 1, 2, and 3 were collected together, and the whole, in the state of nitrates mixed with five times their weight of saltpetre, was submitted to fractionated fusion between 400° and 420°. There were thus obtained six new fractions (Series II.), and a portion not decomposed, No. 7.

	Numbers (Series II.)	Atomic weights.
Between 400° and 430°	1	135·6—135·1
	2	140·4
	3	142·6
	4	142·9
	5	142·5
	6	141·25
Nitrate not decomposed	7	140·1

Thus the curve of the atomic weights presents two branches, the one ascending, the other descending, with a maximum for No. 4 close upon 143. This anomaly is due to the presence in the first fractions of a certain quantity of earths not belonging to the ceric group. On eliminating these earths by a saturated solution of potassium sulphate, we re-ascend for the precipitated part to a number close upon 143.

Nos. 4 and 5 (Series I.), re-united, were again fractionated by melting the nitrates with 5 parts of saltpetre at 400° and 430°.

	Fractions (Series II.)	Atomic weights.
From 400° to 430°	1	142·15
	2	141·99
	3	141·7
	4	141·48
Nitrate not decomposed	5	138·7

The same has been done with the fractions 6, 7, 8 (Series I.), re-united.

	Fractions (Series II., set 2).	Atomic weights.
From 410° to 430°	1	141·0
	2	141·1
	3	140·5
From 430° to 460°	4	139·4
	5	138·5
	6	138·1
	7	138·0
Nitrate not decomposed	8	138·0

We then re-unite the earths which after the second fusion with saltpetre have given atomic weights between 142 and 143.

	Fractions (Series III.)	Atomic weights.
Between 400° and 420°	1	142·8
	2	143·0
	3	142·8
	4	142·5
Nitrate not decomposed	5	141·6

The earths which after Series III. have given atomic weights above 142·5 are re-united, and divided into two fractions by fusion between 400° and 420°.

Fractions (Series IV.)	Atomic weight.
1	142·8
2	143·1

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* See *Comptes Rendus*, cxx., p. 962, and Chem. News, lxxi., p. 260.

It seems, therefore, that we have reached the limits of the separations, and that the didymium 143 to 143·1 represents that with the highest atomic weight. No. 1 (Series IV.), which gives 142·8, has been further brought by fresh separations to a product showing 143·3.

We have thus fixed approximately the highest atomic weight of didymium between 143 and 143·5.

The treatment of monazite, conducted almost like that of cerite, has yielded, among the earths separated between 410° and 460° by melting the nitrates with saltpetre, an oxide which, after a careful elimination of the bases alien to the cerite group, gives very rose-coloured salts, showing the absorption rays of neodymium, and giving for the atomic weight of the corresponding metal a value close upon 137·5.

I have reason to think, after numerous experiments into the details of which I cannot here enter, that between these two limits, 137·5 and 143·5, there come other earths all showing the properties of didymium, especially an earth the atomic weight of whose metal will be close upon 140. It may still be possible that this last earth may be divided into the two extremes by suitable procedures. For the present we leave this question open.

In the foregoing we have disregarded praseodymium, the salts of which are green, and which on our methods of separation has revealed itself only by the absorption-rays.

Some experiments in course of execution have also shown us that lanthanum oxide (defined as above) may be resolved into at least two earths, one of which would have for the atomic weight of its metal a number near 138, whilst the other would have a value near 135. This latter point will form the object of a closer investigation.

As for the didymiums, the nitrates present a resistance to decomposition in the inverse ratio of the atomic weight. The earth with the lowest atomic weight accumulates in the latter parts of the treatment.

In the whole of these researches I have again utilised as means of separation:—1. The fractionated crystallisation of the sulphates in heat; the sulphate corresponding to the lowest atomic weight accumulates generally, as in the case of cerium, in the mother-liquors. 2. The different solubility, in cold and heat, of the double potassium sulphates, which present the same peculiarity.

These experiments will be continued in the hope of explaining the questions left doubtful, and of doing away with the marks of interrogation put in the bulky record of my numerical determinations.

The question must also be studied from the spectroscopic point of view. In the above we have taken as a criterion the atomic weights aided by the absorption spectra.—*Comptes Rendus*, cxx., p. 1143.

THE DECARBONISATION OF BONE-BLACK.*

By WILLIAM D. HORNE, Ph.D.

The chief value of the enormous quantities of bone-black annually used in refining sugar, glucose, mineral and other oils, &c., lies in its power to withdraw from solutions the contained organic colouring matters. After the liquid under treatment has run for some time over the bone-black, the absorption of colouring matter by the latter is seen to diminish, and when this has proceeded to a certain point the supply is cut off and the bone-black subsequently washed with water, naphtha, or other appropriate solvent to wash out, as far as possible, the colouring matters, &c., which have been absorbed by the bone-black. In spite of the most careful washing, however, some carbonaceous matter persistently clings to the char, to remove which the bone-black is heated in closed iron pipes or retorts in kilns without the access of air. A destructive distillation of the carbonaceous matters results, driving out a large proportion of their substance in gaseous form, but still leaving a small quantity of their carbon deposited in the pores of the grains of bone-black. This accumulation of carbon is quite slow, and the char may be used about a hundred times in refining high grade sugars before its pores become so thoroughly choked as to destroy its usefulness. The deterioration is more rapid for low grade sugars; and in refining petroleum the deterioration is so excessive that a dozen treatments will often exhaust the char. Thus the sugar refiner finds his char exhausted in about a year, and the oil refiner much sooner. Other minor changes take place in the char, of course, but none which can compare in destructiveness to this accumulation of carbon.

When it is remembered that about three tons of bone-black are needed in a sugar refinery to each ton of sugar represented in the daily melt, and that while new bone-black costs upwards of forty dollars a ton, the discarded char brings only about one-third of that price, it will be appreciated what a heavy annual investment the purchase of new bone-black entails. Some unsuccessful attempts to obviate this difficulty had been made by others, but the distinction of overcoming it belongs to Mr. Moriz Weinrich, who is already world-renowned as the inventor of the steam washing centrifugal machine which bears his name.

He has recently invented and patented processes and apparatus for radically improving the quality of old bone-black. One process consists of the complete removal of carbon from the bone-black, and the artificial introduction of fresh carbon in smaller quantity. The other consists of a uniform partial removal of carbon when that element is excessive. The first is applicable to exhausted char, such as sugar refineries and oil refineries discard. The second is preferable for removing small percentages of carbon from bone-black which has begun to deteriorate through the choking of its pores with carbon, but which has not reached the limit of usefulness. In the first case all of the carbon is burned out by passing the bone-black in a small continuous stream through the inventor's apparatus, a nearly horizontal cylinder of sheet-iron, which is heated to a dull red and rotated constantly. The char enters the drum through a central orifice in the head closing one end, which is slightly higher than the other, and leaves the drum through peripheral openings in the head of the lower end. Within the drum longitudinal projecting ribs serve to expose the bone-black more completely to the hot air in the drum. The air enters at the openings in the lower end of the drum and either wholly or partially oxidises the carbon in the bone-black, depending upon the heat of the drum, the volume of air, the amount of bone-black fed into the drum, the speed of turning, &c.

In case the carbon is all removed, the mineral frame-work remains intact with its pores opened up. This bone-black can then be treated with a solution of glue, molasses, or or other carbonaceous matter to thoroughly impregnate it. Then the whole can be rendered thoroughly dry and submitted to destructive distillation in closed retorts without the access of air. The organic matter is hereby charred in the very pores of the grains of bone, and the carbon thus deposited seems to be exactly similar to that originally present. After the above re-carbonisation the grains must be washed with hot water to remove soluble substances, and then the char is ready for use.

In the case of partial decarbonisation, only one operation—that of passing through the drum—is necessary, where a high carbon char can be reduced to a low carbon char, and the process regulated to remove any percentage required. Washed char, fresh from the filters, and containing those organic matters which are usually destroyed by destructive distillation in retorts or kilns, can be thoroughly cleansed by passing it through this apparatus at a heat below redness which indicates the possibility of this method replacing the present method of purification or revivification in kilns.

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* Read before the New York Section of the American Chemical Society, April 12, 1895.

These methods have been investigated and tested by the author in the laboratory and on a working scale in their relations to sugar refining, with eminently satisfactory results, as shown below. Some unfavourable results have at times appeared, but they have been due to removable causes, or have been so slight as to be negligible in consideration of the great advantages attained.

A quantity of old bone-black discarded from a sugar refinery, and containing in the neighbourhood of 20 per cent of carbon, was heated in the open air until it was burnt white. Sufficient low grade sugar syrup for its dry substance to be equal to about 15 per cent of the weight of the decarbonised char was diluted with hot water and then thoroughly mixed with the burned bone, then evaporated to dryness, and put into an iron tube closed at one end and having only a small vent in the cap at the other end, and heated to a dull red until all the gas was given off. This carbonised bone was then cooled and washed with water, to remove all soluble matter, and dried. It now resembled new char in appearance, but contained only about 5 per cent of carbon. 300 c.c. of this char was put into a litre bottle with 350 c.c. of a solution of molasses-sugar, 33° Bé. and exponent or coefficient of purity equal to 89·2, and heated one and a half hours in a water-bath at 175° F. with frequent agitations. New char was washed similarly and dried and subjected to the same treatment. The solutions were then filtered off, and while both had been greatly lightened in colour, that from the re-carbonised char was considerably lighter than that from the new char. The exponent of the former was 93·0; that from the latter 92·4. The char samples were carefully washed and heated in closed tubes, as before, to remove the impurities, and again treated as before. In all these two samples were submitted to nine successive treatments with very dark sugar solutions, the object being to ascertain whether the artificially carbonised char would stand use as well as ordinary char; and it was found that while both samples deteriorated greatly owing to the large amount of work which had been put upon them, the treated char was relatively as much better than the other sample at the end as it had been at the beginning so far as colour was concerned.

The new char had increased the exponent 0·17 per cent more than the treated char in the average of all nine tests; but while the new char had removed 66·6 per cent of the colour from the average solution, the re-carbonised char had removed 83·3 per cent.

A decarbonising apparatus was built consisting of a cylindrical drum of $\frac{3}{16}$th-inch wrought iron 9½ feet long by 2½ feet in diameter, with a central longitudinal shaft by which it is turned. The drum has a slight inclination from the horizontal, and is provided with internal longitudinal ribs to raise the char a little way on the ascending side as the drum revolves. The whole is enclosed in brick-work and heated by a fire built beneath its lower end. By means of this either a total or a partial decarbonisation of char can be effected, and the amount to be burned off can be regulated to a nicety by proper adjustments.

Bone-black that had been in constant use nearly a year, and containing 12 per cent of carbon, was reduced to about 9 per cent of carbon and tested in the laboratory against the untreated char by the above-mentioned filtration process. The original solution used had a colour equal to 200 on an arbitrary scale. The filtrate from the untreated char had a colour of 80, and that from the treated char a colour of 27. In another test the original solution had a colour of 240.

Filtrate from untreated char	110
,, treated ,, ...	20
,, overtreated char (some white grains) ..	26

The same samples of char, after draining, were treated again with a slightly less amount of sugar solution.

Filtrate from untreated char, colour = ...	120
,, treated ,, ,, ...	40
,, overtreated char ,, ...	50

In the two treatments the—

Untreated char	removed	52·5	p. c. of	the colour present.
Treated	,,	87·9	,,	,,
Overtreated	,,	84·5	,,	,,

It was thought that these tests, extending over one and a half or two hours, might show a greater difference between the samples than tests extending over a longer period, and so the following experiment was made:—

300 c.c. of each char was heated at 175° F. with 600 c.c. Muscovada sugar solution at 27° Bé., giving the following results. The original solution had a colour of 210.

	1½ hours.	6 hours.
Filtrate from house char, colour =	50	12
,, new ,, ,,	40	10
,, treated ,, ,,	20	7

Showing that the treated char held its own very satisfactorily. Further, a series of six consecutive treatments of new char, char several months in use, and the same after partial decarbonisation, was made. 300 c.c. of each black was heated at 175° F. with 600 c.c. Muscovada sugar solution at 27° Bé. for ten hours, being shaken every fifteen minutes. The char was thoroughly washed, and heated in nearly closed tubes after each absorption test. The average colour of the liquor going on was 152·5, and that coming off was—From the house char, 22·8; from the new char, 16·4; from the treated char 16·7. The treated char, although a trifle below the new char in the final average, actually deteriorated less during the test than either of the others, and thus showed a relative improvement at the end of the experiment.

Many tests have been made on the working scale which have demonstrated the superiority of the decarbonised char over old char, and its equality in many respects to new char. In the first of these tests a filter of house char containing 12·32 per cent of carbon, and another of decarbonised char containing 10·04 per cent of carbon, had equal quantities of the same liquor run over them for a prolonged period, forty-nine and a quarter hours. The average liquor from the house char had a colour of 25, while that from the treated char had an average colour of 15; and it was very striking that the difference in colour increased as the test proceeded, the latter part of the liquor from the untreated char averaging 50, while the corresponding portion from the treated char averaged only 25. The house char withdrew 79·88 per cent of the colour present, while the treated char withdrew 87·69 per cent. In another set of filtrations on the working scale in a sugar refinery a raw sugar solution, colour 120, Bé. 27·7°, and exponent 90·09, was put in the regular course of running through filters of char respectively several months old, new and decarbonised. The average colour of that from the old char was 23, from new char 19, from the partially decarbonised char 18. The exponents scarcely varied, being respectively 92·17, 92·37, 92·09.

These are a few of a great many tests, both in the laboratory and in the factory, made upon char which had been partially decarbonised in a small working model which could not be controlled with the desired nicety, while the average percentage of carbon in the decarbonised char was 10·04 per cent, or 2·28 per cent less than in that from which it was prepared, there was a good deal of it which through different causes still contained more than 11 per cent of carbon, and considerable which had been so overburned as to be rendered weak as a decolouriser. These two extremes, while giving a favourable-looking average percentage of carbon, both deteriorated the char for the purposes in hand. Some improvement having been made in the operation of the decarbonising drum, which, however, is still far inferior to what the inventor's design calls for, it has been possible to turn out a much more uniform product. The carbon can be reduced to any desired point and kept to within ½ per cent of the requisite figure. Having thus prepared another large quantity of char, sufficient for factory tests, another experiment was made. The carbon this time was reduced from 13·03 per cent to 10·22 per cent, and two filters filled with these grades were run against each other. The liquor entering had a colour of 110. The average of that coming from the untreated char was 10, while that coming from the treated char, all the conditions being carefully kept precisely similar, was only 5. From the old char the liquor ran water-white for less than one hour; from the decarbonised char it ran water-white for more than five hours, and at the end of the run the liquor from this filter was only about as dark as that at the middle of the run from the filter of ordinary char.

Now, as to the changes in the bone-black itself after a partial decarbonisation. Microscopic examination shows the decarbonisation to be uniform throughout the grain. Two analyses made to illustrate the chemical changes may be quoted:—

	Before decarb. Per cent.	After decarb. Per cent.
Carbon	12·32	8·90
Calcium carbonate ..	3·32	3·26
Iron	0·32	0·21
Calcium sulphate . ..	0·904	0·877
,, sulphide . ..	0·628	0·494

The most noticeable, and in fact the most desirable, changes are the reduction of carbon with a corresponding opening of the pores and increase in absorbing power, and the reduction of calcium sulphide, which is very important for sugar refineries, in view of the deleterious action this substance exercises upon the sugar. Numerous experiments showed that the carbonate of lime is not decomposed by the mild heat which suffices for oxidising the carbon, and the slight decrease indicated above is doubtless due to variations in samples or error of analysis. The friction of the grains of bone-black against each other in the drum is so slight that very little dust is formed. Samples taken to represent as nearly as possible the same char before and after treatment showed percentages of dust as follows:—

	Before treatment. Per cent.	After treatment. Per cent.
Finer than 30 mesh ..	12·56	12·64
,, 50 ,, ..	0·96	2·20

The bone-black becomes specifically lighter in proportion to the carbon lost, but this does not show in the determinations of sp. gr. probably because of the grains packing more closely after treatment. This indicates a wearing off of some sharp corners of the grains. A quantity of bone black, which before treatment had a sp. gr. of 1·0624 and lost 2 81 per cent of carbon during treatment, had a sp. gr. of 1·0636 afterward.

As might be expected, the process of opening the choked pores renders the bone-black slightly more friable, as shown by the fact that a sample which before treatment gave 1·76 per cent of dust by the method described by the author in a previous paper (Chemical News, lxxi., p. 42), gave 2·84 per cent after treatment. This, however, is scarcely more than is given by some new bone-blacks.

The great advantages of these inventions, then, are quite apparent. The refiner of oil, sugar, or glucose who uses large quantities of bone-black need not discard it at a great loss after its pores are choked with carbon and its decolourising power lost; but he can, by a very simple and inexpensive process, bring it back to its original decolourising power, when it will last nearly, if not quite, as long as before. But by far the greater advantage is the possibility of preventing its ever getting into bad condition by submitting it to the decarbonising process while yet the carbon is only slightly above the normal for new char, and thus keeping it always at its maximum efficiency.

By a careful use of this apparatus it is possible to burn off the organic impurities persisting in bone-black after washing instead of charring them as in the ordinary method of revivifying in kilns with the exclusion of air; and it is not at all impossible that the apparatus will in the near future supersede the present kilns used in all factories employing large quantities of bone-black.

Yonkers, N.Y.

ON INDISCRIMINATE "TAKING."

By PETER T. AUSTEN.

In many of the text-books which have of late appeared, and even in articles by some of the most renowned chemists, the verb "to take" is frequently used in a way that is very annoying to teachers who are endeavouring to train students in brevity and exactness of expression. Pages could be filled with examples of bad style and verbosity that ill accord with the clearness and brevity that are desirable, and that are supposed to characterise scientific literature. A few quotations from recent text-books will suffice ao illustrate this particular case—that of indiscriminate "taking."

"Take a cylindrical porous jar, such as is used in a galvanic battery, close the open end," &c.

It were better to say—"Close the end of a cylindrical porous jar, such as is used," &c.

Another example—"Take two flasks and connect them."

Better—"Connect two flasks," &c.

Another—"The method of experimenting adopted by Graham was to take a bottle or jar with a neck contracted somewhat and fill it to within half an inch of the top with the solution of the salt to be investigated."

Better—"The method . . . was to fill a bottle or jar with a somewhat contracted neck to within half an inch," &c.

Another—"If we take an iron tube closed at one end and connected at the other with a Sprengel pump and exhaust it completely."

This awkward form of diction often excites mirth in the class room, as it gives unusual opportunities for double meanings.

"Take a pound of sugar and an equal weight of sulphuric acid." This would be a severe dose even for a trained scientist.

The following is from a recent text-book—"Take a lump of chalk or sandstone, some very dry sand, a glass of water, and a glass of treacle."

This might do for a bill of fare in a Chinese restaurant, but it is out of place in a scientific book.

"Take some white arsenic,"—"Take a seidlitz powder,"—are the singular directions which preface two experiments in a book recently published by the Society for Promotion of Christian Knowledge, London.

If editors and teachers will pay more attention to this awkward use of the word "take" they will incur the gratitude of a patiently suffering public.—*Science.*

Polytechnic Institute of Brooklyn.

"Who Discovered the Circulation of the Blood?"—An amusing story was recently told by a lecturer who perambulates the country giving popular lectures on Physiology in rural parts. The chairman upon one occasion was a clergyman, who, knowing nothing of the subject of the lecture—namely, "The Circulation of the Blood"—hurriedly consulted a cyclopædia before taking the chair. He introduced the lecturer as follows:—"Ladies and gentlemen,—You are going to-night to listen to a lecture on the heart and the circulation of the blood. Perhaps you would like to know who invented the circulation. The circulation was invented by a person of the name of Harvey, and if you are anxious to know who Harvey was I can tell you that he wrote the 'Meditations amongst the Tombs' and discovered Harvey's sauce for fish."—*Medical Press and Circular.*

CORRESPONDENCE.

THE USE OF THE TWADDELL SCALE FOR SOLUTIONS LIGHTER THAN WATER.

To the Editor of the Chemical News.

Sir,—In a review appearing in the Chemical News (vol. lxxi., p. 268) on Redwood's "Theoretical and Practical Ammonia Refrigeration," appear the words:—"Of course Twaddell, being only adapted for solutions specifically heavier than water, cannot be used for ammonia." There appears to me no reason why Twaddell should not be adapted for solutions lighter than water, as follows:—

1·005 sp. gr. = +1° Tw.
1·000 ,, = 0° ,,
0·995 ,, = −1° ,, &c.

There is no reason, as far as I can see, why we should not have minus degrees Twaddell for solutions lighter than water in the same way that we have minus degrees Centigrade for temperatures below the freezing-point of water. The Twaddell hydrometer for the minus degrees could be marked in red letters on the stem to distinguish them from the plus degrees. The reading for minus degrees would be read from the bottom of the stem upwards. The rule for the conversion of degrees Twaddell into specific gravity would become—

$$1000 \pm x^{\circ}. \times 5.$$

By this means "our old enemy Baumé" might be easily dispensed with.—I am, &c.,

Clayton Beadle.

VOLUMETRIC DETERMINATION OF SUGAR BY AMMONIO-CUPRIC SOLUTION.

To the Editor of the Chemical News.

Sir,—In the Chemical News for May 24 (vol. lxxi., p. 257) my assistant and demonstrator, Mr. Peska, and myself, who communicated Mr. Peska's paper to the Chemical Society, are charged with unjust action by Mr. Allen, who says that we have "appropriated" and "annexed" his scientific idea, namely, the discovery that a layer of mineral oil protects an ammoniacal cupric solution from oxidation by air. In agreement with Mr. Peska, I beg to answer as follows:—

The above method was practically used by Mr. Peska in October, 1893, as I can prove, if necessary, by trustworthy scientific witnesses. The original paper of Mr. Allen was *not known* to me or to Mr. Peska, for *The Analyst* is inaccessible to us, and I am sorry to say that my time and scientific occupation do not allow me to read other than first-class English chemical journals, the rest being known from abstracts only. So I know Mr. Allen's paper on the "Examination of Urine for Small Quantities of Sugar" only from an abstract in the *Chem. Soc. Journ.*, Dec., 1894, p. 488. The abstractor does not refer to the use of mineral oil, being probably not struck by the great scientific importance of that discovery.

I confess I had no wish to read a paper in full, the end of which contains the "novelty" that the best test for traces of sugar in urine is the well-known phenylhydrazine.

Mr. Peska, in his original paper, and in my abstract of it, speaks of Fehling's method or its rather lengthy modification by *Soxhlet.*" The change of the last name for *Allen* I regard as a misprint which might be explained by one of the Secretaries of the Chemical Society, *who alone* are responsible for the abstracts in the *Proceedings*. I got no letter from the Secretary on that point whatever.

Mr. Peska's intention was certainly not to quote all papers on the determination of sugars, and especially not of sugar in urine, as that of Mr. Allen, for it alone would have filled several pages and would be of no use. If the manipulative device found by Peska in 1893 was not published *at once*, it is owing to a principle of our laboratory to publish scientific work after some results worth publishing are obtained, even if it may take ten years or so. The otherwise practical device of using vaseline oil I do not consider to be the principal merit of Mr. Peska's paper; I see it in the fact that he has minutely worked out a method, not only of determining *sugar in urine*, but of accurately determining glucose, invert sugar, same in presence of saccharose, then maltose, lactose in solutions of all concentrations, and of studying the interesting behaviour of dextrines, as will be seen soon from the full paper.

I should have never entered into the discussion of the mere priority of the use of vaseline oil had I not been attacked by Mr. Allen. Instead of charging us with dishonest action, Mr. Allen had better sent me a copy of his paper and I should have given him private information. I should have given him all possible satisfaction if I had found that his method is so beautifully worked out that it makes Mr. Peska's paper superfluous. I conclude, however, from the said abstract that there is a great difference in this point between the paper of Mr. Allen and that of Mr. Peska.—I am, &c.,

Bohuslav Brauner.

Bohemian University, Prague,
June 2, 1895.

"STEEL WORKS ANALYSIS."

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lxxi., p. 268) there appears a letter from my friend Mr. William Galbraith in which he suggests that I was unintentionally unfair in my criticism ("Steel Works Analysis," p. 152) of his admirable process for the volumetric determination of chromium in steel. He seems to object to the expression "modified method," although in the same paragraph it was stated that as far as possible the simplicity of the original process had been preserved. As Mr. Galbraith surmises, I had no intention of being unfair, and after carefully considering the matter have come to the conclusion that Mr. Galbraith has no ground whatever for complaint. As he says, I am "anxious that the process should live," and, consequently, I have made a very large number of experiments on the method and devoted six pages of my book to its consideration. Practically, the whole matter lies in a nutshell. Mr. Galbraith, in his original method, advised the use of about 1¼ grms. excess of permanganate, or about six times too much. He oxidised in 60 to 70 c.c. of liquid containing 18 grms. of strong sulphuric acid. Under these conditions, in steels containing 2 or three per cent of chromium, the results are always seriously low: First, because the large manganic precipitate always carries down some chromium with it; second, in a solution so strongly acid, the complete oxidation of Cr_2O_3 to CrO_3 is practically impossible.

Some two or three years ago I modified the process (and at the meeting of the Sheffield Metallurgical Society fully described the modification in Mr. Galbraith's presence) by employing only 0·2 grm. excess of permanganate, and oxidised in a total volume of about 150 c.c.; under these conditions the results are accurate. In fact the alterations which Mr. Galbraith objects to as being so "trivial" and "unfair" as not to constitute any "modification" (I know of no other word to use), determine the difference between reliable and worthless results.

With reference to Mr. Galbraith's new soda process, it is certainly the general impression that he designed it to replace the old method, and that it was applicable to chrome steels.

Mr. Galbraith mentions the fact that Mr. Stead has described a modification of the permanganate process. If Mr. Galbraith will take the trouble to refer to p. 157

et seq. of "Steel Works Analysis" he will find this process favourably criticised and fully described.

Mr. Galbraith is evidently hyper-sensitive to criticism, even of the mildest description, and his own florid denunciation of my gravimetric process seems to have escaped his memory. He declared at the meeting of the Sheffield Metallurgical Society, to which he refers, that the method gave results "50 per cent too high"—a rash assertion, which the personal experience of several steel work's chemists present, to say nothing of my own exhaustive experiments, proved to be absolutely inaccurate.

Steel chemists are much indebted to Mr. Galbraith for devising the broad principle of a rapid and beautiful volumetric method for the estimation of chromium in steel. Unfortunately, however, the process is essentially empirical, and its success depends on a rigid adherence to special details; the latter were not accurately described by Mr. Galbraith, and, in consequence, many chemists abandoned the method as unreliable. Now, because I have endeavoured to restore confidence in the process by pointing out where it may go wrong, and how to avoid error, Mr. Galbraith, so far from being grateful, considers I am "unfair." I am content to leave the matter to the judgment of steel work's chemists.—I am, &c.,

J. O. Arnold.

The Technical School, Sheffield,
June 10, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 21, May 27, 1895.

Nomination of a Foreign Associate.—The Academy proceeded to nominate a foreign Associate *vice* the late Professor Van Beneden. The number of voters was 48. Dr. E. Frankland received 43 votes; Prof. Sir G. G. Stokes, 3 (!); Mr. Newcomb, 1; Herr Suess, 1. Dr. Frankland having obtained an absolute majority of the votes was proclaimed elected.

The Academy then proceeded to nominate a commission to draw up a list of candidates for the position of Foreign Associate *vice* the late Herrn von Helmholtz. The commission includes three members on behalf of the sections for mathematical sciences, MM. Bertrand, Fizeau, and Tisserand, and three on behalf of the sections for physical sciences, MM. Berthelot, Daubrée, and Van Tieghem.

Contribution to the History of the Earths of Cerite.—P. Schützenberger.—(See p. 288).

Accumulation in the Soil of Cupric Compounds used to Combat the Parasitic Diseases of Plants.—Aimé Girard.—The author concludes from a numerous series of experiments that the prolonged use of the compounds of copper for the treatment of the vine or the potato has no effect either upon the quantity or the quality of the produce.

Reduction of Nitric Oxide by Moist Iron or Zinc.—P. Sabatier and J. B. Senderens.—The simultaneous formation of free nitrogen and of nitrous oxide is not established. The nitrous acid falls gradually from 68 per cent during the first hour to 0·0 after a month. The free nitrogen rises from 32 during the first hour to 75·3 from the fourth to the fifth day, and then falls; after one month to 63·1; and after two months to 48. The hydrogen increases from 1·7 from the second to the seventeenth hour to 52 after two months.

The Reduction of Silica by Aluminium.—M. Vigoreux.—It appears that there are two modifications of silicon, the one amorphous and the other crystalline and in thin layers transparent.

Certain Reactions of Lead Sulphide.—A. Lodin.—Lead sulphide enters into fusion only at 935°, but its vapour tension is considerable at much lower temperatures. This latter property explains the phenomena of volatilisation ascribed by Hannay to the hypothetical compound PbS_2O_2, as also to the active development of the reactions of PbS upon PbO and $PbSO_4$ at temperatures below 935°. At these temperatures the formulæ admitted long ago to explain the reactions of the metallurgy of lead are exactly verified.

On the Campholenic Derivatives.—A. Béhal.—The author considers the active and inactive campholenic acids as stereoisomers.

On Crystalline Cinchonicine.—Ferdinand Roques.—This substance has hitherto been known only as vitreous and resinoid, but the author has obtained it in anhydrous amber-yellow crystals, forming crystals of often more than 10 m.m. in length by 3 m.m. in breadth, but presenting curved surfaces. Their optical properties indicate a triclinar form. They are soluble in benzene, toluene, acetone, chloroform, and alcohol (absolute or aqueous), but they have not hitherto been re-crystallised from these solutions. The author is continuing his researches, and extending them to quinicine.

Transformation of a Salt of Aniline into Acid Aniline.—L. Simon.—The author maintains anilephenylglyoxylic acid is entirely transformed by boiling water into aniline phenylglyoxylate.

On Ozobenzene.—Adolph Renard.—Ozobenzene is an addition product in which the six supplementary atomicities of the benzenic nucleus are saturated by six atoms of oxygen connected to each other two by two, one atomicity.

The Fixation of Iodine by Potato-starch.—Gaston Rouvier.—Whilst the starches of wheat and of rice, produced by one and the same vegetable family, behave in the same manner with iodine, that of the potato, produced by a very remote family, behaves in a totally different manner.

Elimination of Magnesium in Rachitic Patients.—Oechsner de Coninck.—The author notices the minute proportion of magnesium eliminated in the urine of the rachitic cases examined.

Journal fur Praktische Chemie.
New Series, Vol. li., Parts. 1 and 2, 1895.

Contributions to a Knowledge of the Arsenites.—A. Stavenhagen.—The author describes here the potassium ortho-, meta-, and pyro-arsenites, besides the two salts $K_2As_4O_7+2H_2O$ and $K_4As_6O_{11}+3H_2O$; the sodium ortho-, meta-, and pyro-arsenites; the ammonium ortho-, meta-, and pyro-arsenites; the corresponding calcium, strontium, and barium salts; the magnesium ortho- and pyro-arsenites; the zinc and cadmium ortho-arsenites; the mercurous and mercuric ortho-arsenites; the copper ortho- and meta-arsenites; the silver ortho- and pyro-arsenites, with Girard's salt, $Ag_6As_4O_3$; the auriortho-arsenite; the thallium ortho-arsenite; the stannous and stannic ortho-arsenites; the lead ortho-, meta-, and pyro-arsenites; the bismuth arsenite; the chromium arsenite; the manganese ortho- and pyro-arsenites; the iron arsenite. It is here remarked that the favourable action of ferric hydroxide in cases of arsenical poisoning is due to the fact that it prevents the formation of hydrogen arsenide. The author further describes cobalt ortho- and pyro-arsenite, and the compound $Co_3As_4O_9+4H_2O$; nickel arsenide; platinum ortho-arsenite, and platinum oxide-ammonium arsenite.

Synthetic Experiments in the Pyrazol Series. Part I.—R. von Rothenburg.

Researches from the Laboratory of the University of Freiburg, in Breisgau.—These researches include a discussion on the isomeric diazobenzene potassium sulphite, by Ad. Claus; and a memoir by Alb. Edinger, on the aromatic amines, sulphidised in the nitrogen.

On Pyro-antimonic Hydroxide. — C. Serono.— The author infers from his researches that the hydrate $Sb_2O_32H_2O$ does not exist.

On Two New Laboratory Appliances. — C. V. Schön.—This paper cannot be abstracted without the insertion of the two accompanying figures.

The Combination-Heat of the Crystalline Water of Organic Compounds.—W. J. Jorissen and E. van de Stadt.—A series of thermo-chemical determinations.

Some Experiments on Oxidation by Partial Combustion.—J. Walter.—Hitherto there was known only a single instance of the production of one substance from another by a partial combustion, *i.e.*, that of formaldehyd from methylic alcohol. The author has been engaged with experiments in this direction, but he has never obtained results even approaching those of formaldehyd.

Remarks on the Work of Curtius and Dedichen: "Synthesis of Benzenehydrazines by means of Hydrazine Hydrate."—A. Purgotti.—Already inserted.

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 5, 1895.

A Regulator of Temperature.—M. Berlemont.—This apparatus cannot be described intelligibly without the accompanying figure.

On Certain Addition-Derivatives of Ferric Chloride and Nitric Oxide.—V. Thomas.—Nitric oxide reacts very slowly in the cold upon ferric chloride, forming a definite brown powder. If the temperature is raised to 40° we obtain a red substance. The compound obtained in the cold consists of $Fe_2Cl_6.NO$. The substance formed at from 40° to 60° consists of $2Fe_2Cl_6.NO$. Both these substances are very hygroscopic. They are decomposed in contact with water, losing the nitric oxide which they have absorbed. They are fusible in sealed tubes without decomposition. If heated in the open air they are transformed into ferric oxide. The author has not been able to obtain them in crystals.

Cyanic Ethers and Nitriles of the Alcohols.—Albert Colson.—The author has exposed to the sun a mixture of washed ether and cyanogen chloride. The product was methane. On exposing the same mixture to the sun during the whole of summer he obtained an isomer, very stable. The author has further obtained cyanal acetate, propionate, and propylcyanal acetate.

MISCELLANEOUS.

The German Society of Applied Chemistry (Deutsche Gesellschaft für Angewandte Chemie) held its Annual Meeting in Frankfort-am-Main on the 9th to the 12th inst.

The Deutsche Electro-Chemische Gesellschaft held its Annual Meeting in Frankfort-am-Main on the 6th, 7th, and 8th inst. Among the papers read at the meeting were the following:—"Charging Accumulators by means of an Alternating Current," by Herr Pollak; "Calcium Carbide," with experiments, by Dr. Borchers; "On a New Method of Analysis by Electrolysis," by Dr. Jordis; and "Electrical Transmission of Power," by Prof. Ostwald. Visits of inspection were also paid to the Accumulator Works of the Pollak Co., and to the Gold and Silver Separating Works in Frankfort.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 10th inst., Sir James Crichton-Browne presiding. The following were elected Members:—Mr. Benjamin Bennett, Mrs. Henry Burton Buckley, and Mr. William Watson Cheyne, F.R.S. The special thanks of the Members were returned to the Right Hon. Lord Playfair for his donation to the Fund for the Promotion of Experimental Research at Low Temperatures.

MEETINGS FOR THE WEEK.

Wednesday, 19th.—Geological, 8.
— Microscopical, 8.
— Meteorological, 7.30.
— Institution of Mining and Metallurgy, 8.
Thursday, 20th.—Chemical, 8. Extraordinary General Meeting to consider change in Bye-law I. The business of the Ordinary Meeting will follow. Ballot for the Election of Fellows. "On Lintner's Isomaltose," by Horace T. Brown, F.R.S., and G. H. Morris, Ph.D. "Transformation of Ammonium Cyanate into Urea," by Prof. Walker, D.Sc., and T. F. Hamley. "Some Derivatives of Humulene," by A. C. Chapman. "Note on Thio-Derivatives of Sulphanilic Acid," by Miss Walter. "The Chlorination of Orthochlorotoluene" and "The Six Dichlorotoluenes," by W. P. Wynne, D.Sc., and A. Greaves. "The Disulphonic Acids of Toluene and of Ortho- and Para-chlorotoluene," by W. P. Wynne, D.Sc., and T. Bruce. "Ethereal Salts of Ethane-tetracarboxylic Acid," by Prof. Walker, D.Sc., and J. R. Appleyard. "Method for Preparing Formyl Derivatives of Aromatic Amines" and "A Modification of Zincke's Reaction," by H. R. Hirst and J. B. Cohen, Ph.D. "New Method of Preparing Cyanuric Acid," by W. H. Archdeacon, B.Sc., and J. B. Cohen, Ph.D.
Friday, 21st.—Quekett Club, 8.

THE CHEMICAL NEWS.

Vol. LXXI., No. 1856.

ON THE
NEW GAS OBTAINED FROM URANINITE.*
(Fourth Note).

By J. NORMAN LOCKYER, C.B., F.R.S.

Continued experiments on the gases obtained by heating the minerals bröggerite and euxenite *in vacuo* have revealed the presence in the spectrum of an important line in the infra-red. By comparisons with the solar spectrum in the first order grating spectrum, the wave-length of the line has been approximately determined as 7065. There can be little doubt, from the observations which have been made, that this new line is coincident with the chromospheric line which occurs in Young's list, having a frequency of 100, of which the wave-length on Rowland's scale is stated to be 7065·5.

It follows therefore that, besides the hydrogen lines, all three chromospheric lines in Young's list which have a frequency of 100 have now been recorded in the spectra of the new gas or gases obtained from minerals by the distillation method.

These are as follows :—

7065·5
5875·98
4471·8

The wave-lengths of the lines are in Rowland's scale, as given in Scheiner's "Astronomical Spectroscopy" (Frost's translation, p. 184). In a partial revision of his chromospheric list, Professor Young gives the *corona* line 5316·79 as also having a frequency of 100 in the chromosphere, but, up to the present, this line has not been observed in the laboratory.

CARIUS - VOLHARD ESTIMATION OF HALOGENS.

By JAMES WALKER, Ph.D., D.Sc., and
JAMES HENDERSON, B.Sc.

We lately recommended the estimation of halogens in organic compounds by the Carius method combined with the Volhard method of silver titration (Chemical News, lxxi., p. 103). Shortly after the appearance of our communication, Dr. F. W. Küster published a paper in *Liebig's Annalen* (cclxxxv., p. 340) on the same subject, in which he rejects the method as untrustworthy. The principal source of error under the conditions employed by him is the action of the excess of silver nitrate on the glass of the tubes, whereby a portion of the silver is withdrawn from the titration, and the volumetric results appear too high. Dr. Küster's interesting observations on the extent of this action are undoubtedly correct, but, as he himself shows, the disappearance of the silver from the solution is largely dependent on the temperature to which the tubes have been heated, the action being very slight at temperatures below 280° and increasing rapidly above 300°. His method of halogen estimation is to heat the sealed tube for two hours at 320° to 340°. In our opinion this temperature is only necessary in very exceptional cases, if a somewhat greater amount of nitric acid is used than Dr. Küster recommends.

Halogen compounds of the fatty series are in general easily decomposed, and it is with aromatic compounds that any difficulty is experienced. We find, however, that if for 0·1 grm. of substance 2 c.c. of nitric acid, of sp. gr. 1·5, are taken, the decomposition is complete after heating for three hours at 250° to 260°, and the action on the glass is so slight as to cause no perceptible difference between the gravimetric and volumetric estimations. The glass we employ is Schott and Co.'s Jena combustiou tubing, which can be easily worked at the blowpipe and is of excellent quality, the same tube bearing repeated heating with the acid. The inner tube, to contain the substance, we make of ordinary hard glass tubing.

Dr. Küster only employs 16 to 20 drops of the 1·5 sp. gr. acid (⅔ to 1 c.c.) to 0·1—0·2 grm. substance, and it probably this circumstance which necessitates the high temperature he employs. As the oxidation progresses water is formed, which dilutes the acid and enfeebles its action. If, therefore, a larger proportion of acid is present from the first, the extent of this dilution is diminished, and the action can be completed at a lower temperature. With 2 c.c. of acid and Schott's glass we have never had a tube burst.

As para-dichlorobenzene was one of the substances with which Dr. Küster experimented, we made one or two determinations of the halogen it contained, both gravimetrically and volumetrically, with the same portion. In no case could the smell of undecomposed chloride be detected on boiling the diluted solution after heating.

I.

0·1459 grm. of para-dichlorobenzene was heated with 0·4049 grm. $AgNO_3$, and 2 c.c. nitric acid, sp. gr. 1·5, for 3½ hours, at 257°. 0·2907 grm. AgCl was obtained, and the filtrate required 7·25 c.c. of sulphocyanate solution (1 c.c. = 0·00812 $AgNO_3$) for complete precipitation.

Chlorine found, gravimetrically.. ..	49·3 p.c.
,, volumetrically	49·5 ,,

The percentage of chlorine in $C_6H_4Cl_2$ is 48·3. The specimen was therefore impure, containing too much chlorine. It was re-crystallised from ether, and another analysis performed.

II.

0·1422 of para-dichlorobenzene was heated as before with 0·4201 grm. $AgNO_3$, and 2 c.c. nitric acid. 0·2796 grm. AgCl was obtained, and the filtrate from this required 10·95 c.c. sulphocyanide solution (1 c.c. = 0·00812 grm. $AgNO_3$).

Chlorine found, gravimetrically.. ..	48·6 p.c.
,, volumetrically	48·6 ,,

The re-crystallisation had apparently effected a considerable purification of the substance.

The following numbers were obtained for para-dibromobenzene, the preparation being from Kahlbaum in Berlin :—

III.

0·1186 grm. para-dibromobenzene was heated as before with 0·2061 grm. $AgnO_3$, and 2 c.c. nitric acid. 0·1903 grm. AgBr was obtained, and the filtrate required 3·35 c.c. sulphocyanide solution (1 c.c. = 0·00982 $AgNO_3$).

Bromine found, gravimetrically.. ..	68·3 p.c.
,, volumetrically	68·7 ,,

The filtrate from the silver bromide was here decidedly turbid. The calculated amount of bromine in $C_6H_4Br_2$ is 67·8 per cent. As in the case of the chloro-compound the preparation contains too much halogen.

We found that the turbidity of the filtrate might be prevented by adding a little concentrated sulphuric acid to the contents of the sealed tube, and the following estimation, with the same compound as before, will serve as an example :—

IV.

0·1203 grm. para-dibromobenzene was heated with 0·2019 grm. $AgNO_3$, 1·5 c.c. nltric acid, and 0·5 c.c.

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* A Paper read before the Royal Society, June 13, 1895.

concentrated sulphuric acid, for 3 hours, at 250°. 0·1943 grm. AgBr was obtained, and the perfectly clear filtrate required 2·65 c.c. sulphocyanide solution (1 c.c. = 0.00983 grm. $AgNO_3$).

Bromine found, gravimetrically..	..	68·7 p.c.
„ volumetrically..	..	68·8 „

The agreement of the numbers obtained by the two methods shows that the action of the silver nitrate on the glass, under the conditions given, is negligible. We venture to think that, if these conditions are adhered to, the Carius-Volhard method may be applied with success to practically all fatty compounds, and to nine out of ten aromatic compounds, if not to ninety-nine out of a hundred.

University College, Dundee.

NOTE ON THE PRODUCTION OF CITRIC ACID FROM CANE-SUGAR.

By Dr. T. L. PHIPSON,
Formerly of the University of Brussels, Member of the Chemical Societies of London, Paris, Antwerp, &c.

I have recently made an experiment at the Casa Mia Laboratory, Putney, which is perhaps worth recording. I have found that an acid, which can be no other than citric acid, is produced in notable quantity by the action of permanganic acid on a solution of sugar in the cold.

Some few grms. of cane-sugar are dissolved in water to which a few drops of sulphuric acid have been added, and a rather strong solution of potassium permanganate is poured in. In a short time, at summer temperature, the solution is white and transparent like water. It is neutralised by addition of a little ammonia, and solution of calcium chloride added. No precipitate occurs, which shows the absence of tartaric and oxalic acids, but on boiling the liquid a precipitate occurs which is soluble in acetic acid, and these reactions are characteristic of citric acid. The precipitate being collected and decomposed with sulphuric acid gave a solution which, on being evaporated, gave small but well-formed crystals, which corresponded in form and properties with those of pure citric acid.

If large quantities of permanganate are used, then a notable amount of oxalic acid is produced at the same time.

The Casa Mia Laboratory, Putney,
London, June 17, 1895.

A NEW METHOD OF STANDARDISING ACID SOLUTIONS.

By E. P. PERMAN, D.Sc., and W. JOHN.

On adding dilute sulphuric acid to a solution of borax, sodium sulphate is formed, and boracic acid set free. One molecule of borax requires one molecule of sulphuric acid to neutralise it, using methyl-orange as indicator. This affords a convenient and accurate method of standardising acid solutions. The following are the advantages of the method:—

a, The quantity of borax required is very large; 5 grms. may be taken for a normal solution, and in that case it is unnecessary for ordinary purposes to weigh to less than a centigrm.

b. Borax is readily obtained pure and keeps well. It effloresces slightly in dry air, and should, therefore, be kept in a well-stoppered bottle; in moist air it remains practically unaltered (see Ramsay and Aston on "The Atomic Weight of Boron," *Trans. Chem. Soc.*, 1893, p. 207).

c. The end of the reaction is shown very sharply.

The borax used was in large crystals, and was bought under the name of "refined borax." The following results were obtained with two solutions of different strengths:—

Borax taken. Grms.	H_2SO_4 solution required. C.c.	H_2SO_4 in 1 litre. Grms.	Standardised by Na_2CO_3 solution. Grms.
20·00	53·85	95·28	95·15
12·54	33·90	94·90	
1·985	25·45	19·00	19·02
2·013	27·21	18·98	
2·015	27·26	18·96	

Hydrochloric acid solution may be standardised in a similar way. The results obtained with this acid are given in the following table:—

Borax taken. Grms.	HCl solution required. C.c.	HCl in 1 litre. Grms.	Standardised directly by Na_2CO_3. Grms.
6·588	22·44	56·10	56·07
7·041	23·99	56·08	56·06
			By Na_2CO_3 solution
3·571	36·82	18·53	18·48
3·571	36·89	18·50	

Boracic acid acts upon litmus or phenolphthalein, so that these indicators cannot be used.

The authors think that the method would prove a very useful one for general laboratory use.

University College, Cardiff,
June 15, 1895.

SULPHUR IN OILS.

By WILLIAM FOX and D. G. RIDDICK.

The following Table gives the mean amounts of sulphur in grains per gallon (by weight) that we have obtained from various oils by burning them by means of a floating wick, such as is used for night-lights, and condensing the vapours given off in a sulphur apparatus in the same way as sulphur is determined in coal-gas. Those oils which do not burn alone were mixed with a sufficient quantity of sperm or cocoa nut oil to make them do so without smoking.

Name of Oil.	Sulphur.
Pure Brown Rape	14·2
Ordinary Brown Rape	17·4
Refined Brown Rape, with sulphuric acid ..	16·8
„ „ „ with Fuller's earth ..	10·0
Ravison Rape	19·1
*Jamba Rape	113·0
Linseed, La Plata	trace
Sperm, pure	2·3
„ Bottlenose	3·1
Cotton-seed	trace
Cocoa-nut, ordinary	3·7
Ground-nut..	none
Neat's-foot	4·7
Olive	none
Cod	5·8
Russian Mineral, 0·908	20·5
Russian Burning Mineral	10·3
American Burning Mineral	16·3
American Burning Water White Mineral ..	8·1
American Burning Safety Mineral	14·0
Scotch Mineral for Gas making	49·8

Liquid Carbonic Acid Works.—Works are being established in Königsberg by a Company known as the Fabrik für Flussige Kohlensäure Oster and Co., for the production of liquid carbonic acid. The plant will have a capacity of 800 to 1000 kilog. per day.

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* Benedikt and Lewkowitsch ("Oils, Fats, Waxes"), state that Jamba oil is free from sulphur.

A METHOD OF DETERMINING THE CRYSTALLISATION OF PRECIPITATES. ZINC AND MANGANESE SULPHIDES, COPPER HYDROXIDE.

By A. VILLIERS

We have already shown that the rate and the temperature of the transformation of amorphous zinc sulphide depend not alone on the composition of the medium in which the precipitation has been effected, but also on changes undergone by this medium after precipitation. Whilst a reduction of temperature retards this transformation, every cause which may produce an effect comparable to a decrease of the dilution of the liquids exerts an inverse action and determines a reduction of the temperature of transformation.

We have thought that the complete congelation of the solvent, being comparable to a concentration carried as far as possible, might enable us to obtain amorphous precipitates in a crystalline state, or at least in an increased state of condensation, notwithstanding the inverse action of a fall of temperature, of slight variations of the ambient medium, involving a variation of the temperature of transformation of more than 100°.

This method seems to be of a somewhat general application, and enables us to obtain easily, by the action of cold, transformations which may be also effected by a rise of temperature, sometimes very considerable. Perhaps these transformations may be ascribed to a different cause, to the compression exerted by the expansion of the ice which imprisons the precipitates. We observe, in fact, after the complete congelation of the liquid produced from the outside to the inside, that the precipitate has been collected in the central part of the block of ice, where it must certainly have undergone a considerable pressure. We have undertaken to ascertain what is the true cause of the transformations thus observed, restricting ourselves at present to giving the three first instances.

Zinc Sulphide.—If we completely freeze the alkaline liquid, holding in suspension amorphous zinc sulphide precipitated from such liquid, and prolong the action of the cold for some hours, we find that, if the liquid is dilute and slightly alkaline after melting the ice, the zinc sulphide is no longer amorphous, and does not re-dissolve, as before the congelation on treatment with a prolonged current of hydrogen sulphide, provided that the volume of the liquid is not too great in proportion to the precipitate.

We may thus, by congelation, transform a precipitate of zinc sulphide, even in media such that the temperature of transformation exceeds 100°.

Manganese Sulphide.—An analogous observation has been made thirty years ago, by Geuther, concerning the transformation of rose-coloured manganese sulphide into the green modification (*Jena Zeits. f. Med. u. Natur.*, ii., p. 127), and, although it has been subsequently contradicted, we have verified its accuracy. To succeed in this experiment we must place ourselves in conditions analogous to those in which the transformation of zinc sulphide is most readily effected. We take a solution of a salt of manganese, *e.g.*, the chloride, very dilute so that the congelation may be as complete as possible, and precipitate it with a very slight excess of ammonium hydrosulphate. The liquid being frozen, and kept at some degrees below zero, the transformation is effected in a complete manner within twenty-four hours.

We may remark that in the same media the same transformation can only be effected by the action of heat at a temperature above 300°.

Copper Hydroxide. — Copper hydroxide is known in various states. If precipitated by an alkali from the solution of a salt of copper, such as the sulphate, it is amorphous, of a blue colour slightly mixed with green, and very unstable. Under conditions which have been studied by several chemists, and especially by D. Tommasi (*Bull. Soc. Chimique*, 1882, xxxvii., p. 197), and to which we shall return, it is transformed into the black oxide.

But the blue oxide and the black oxide may themselves exist in several states representing different condensations. We shall subsequently study these conditions in which the successive transformations are produced,—conditions similar to those which we have found in studying zinc sulphide. At present we shall restrict ourselves to indicating a transformation of the blue copper sulphide which may be obtained by the foregoing method.

Peligot (*Ann. de Chim. et de Phys.*, Series 3, lxiii., p. 347, 1861), on precipitating, under certain conditions, salts of ammoniacal copper, by an alkali or by water, obtained a copper oxide, $CuOHO$, differing from the ordinary blue oxide by its crystalline state, its beautiful turquoise-blue colour, and its very great stability, which render it fit for industrial applications.

This substance may be easily prepared by the transformation of the ordinary hydroxide. If we prepare the latter in the cold by precipitating a solution of copper sulphate not very concentrated, and washing the precipitate with ice-water, the oxide thus obtained presents under the microscope the aspect of a completely amorphous mass having no action upon polarised light. If we freeze the liquid which holds the precipitate in suspension, and keep the temperature below zero, we find that in two hours the crystallisation of the precipitate is much advanced, and the action upon polarised light is very manifest. After several hours the transformation is complete, and the amorphous precipitate is transformed into small dense crystals, presenting the composition and all the characters of Peligot's oxide.

It is probable that some crystalline minerals may thus have been produced by the action of cold. In the course of this investigation we shall find a great number of similar cases.—*Comptes Rendus*, cxx., p. 322.

ACTION OF FLUORINE UPON ARGON.

By HENRI MOISSAN.

The beautiful discovery of argon by Lord Rayleigh and Prof. Ramsay serves to prove that the gaseous bodies, as well as the solids which we encounter in Nature, may contain in very small quantities elements hitherto overlooked. This gas argon presents further a character quite special, for its chemical activity is almost *nil.* Its physical properties have permitted its detection, its preparation, and its study.

Prof. Ramsay, having had the kindness to give me 100 c.c. of this argon, to endeavour to combine it with fluorine, I have been able to perform upon this new gas some experiments which I shall briefly describe.

For some years I have taken occasion to study several simple substances which, under given conditions of temperature, combine with nitrogen very energetically. Such are especially boron and titanium.

I heated titanium, as pure as possible, in an atmosphere of argon, to the temperature at which ordinary glass softens. After heating for thirty minutes there was no decrease of volume, and consequently no probable combination. The titanium had not changed in its appearance.

Pure boron, prepared by means of magnesium heated in a bell of Bohemian glass, did not combine with argon, whilst under the same conditions it united with nitrogen, forming solid boron nitride.

This argon, heated in presence of lithium, does not decrease in volume, yet it is known that under this condition nitrogen rapidly yields a solid lithium nitride, as M. Ouvrard has demonstrated (*Compt. Rend.*, cxiv., p. 120).

The curious decomposition of clèveite by sulphuric acid led me to examine if uranium had any action upon argon. A volume of argon, measured at the mercurial trough, was heated in a small bent tube of common glass along with several fragments of uranium. After heating for twenty minutes the volume of gas was not modified. The uranium had been prepared in the electric furnace, and contained 3·5 per cent of carbon.

To study the action of fluorine upon this new simple substance I made use of the following apparatus :—

A cylinder of platinum, of 10 c.m. in length and 2 c.m. in diameter, is closed by two metallic supports holding discs of transparent fluor-spar with parallel surfaces. On the sides there enter two small tubes of platinum, the one conveying fluorine and the other argon. These two tubes open opposite to each other. A third tube, placed at the end of the cylinder, allows the gaseous mixture to escape. Small metal cocks enable the apparatus to be closed without being able to exert a strong pressure. Lastly, a metallic rod, insulated by the transparent plate of fluor-spar which it traverses, allows the spark of an induction coil to be made to strike in the interior.

The metal supports which contain the discs of transparent fluor-spar, as also the ends of the tubes, are tightened by means of screws which crush upon a small ring of lead placed at the edge of the two tubes to be connected.

The platinum cylinder, dried with care, which had served for preparing pure fluorine, and which has been described (*Annales de Chimie et de Physique*, Series 6, xxiii.), was placed at the end of the apparatus.

All the air of the apparatus was swept out by passing through it 3 or 4 litres of fluorine. The gas which was liberated occasioned no fume in the air, and gave a lively incandescence with silicon. The current of fluorine was stopped, and the argon was introduced through the other platinum tube, being gently displaced by mercury in a small bell fitted with a cock. When the very slow current of argon gas arrived into the fluorine no visible phenomenon was produced. On holding the tube in the fingers no change of temperature was felt.

The electric spark was made to strike into this mixture of argon and fluorine, but it produced no apparent reaction.

The experiment was re-commenced twice, so as to vary the proportions of argon, and the results were still negative.

The difficulty of manipulating fluorine did not allow us to try if a change of volume might ultimately ensue by the action of a series of sparks.

The conclusion which we draw from these experiments is, that at the ordinary temperature, or under the action of the induction spark, a mixture of fluorine and argon does not enter into combination.— *Comptes Rendus*, cxx., p. 966.

THE ACTION OF HEAT UPON ETHYLENE.*

II.

By VIVIAN B. LEWES,
Professor of Chemistry at the Royal Naval College, Greenwich.

(Concluded from p. 287).

SOME information can be obtained as to the secondary reactions which accompany the main decomposition by studying the proportions in which the products, other than ethylene, are present in the gases after heating.

Taking the experiments made upon the effect of length of heated tube and rate of flow, and tabulating the percentages of saturated hydrocarbons and hydrogen corrected for change of volume, we obtain the following results :—

Saturated Hydrocarbons.

Length of tube heated.	1 inch.	6 inches.	18 inches.
5 c.c.	43·72	63·42	70·13
15 c.c.	38·02	44·44	60·46
40 c.c.	25·12	39·16	55·37

The temperature employed in these experiments is not sufficiently high to cause any large amount of the methane to decompose, so that the volume should, according to theory, approximate to two-thirds of the ethylene decomposed.

Rate of flow per minute.	Ethylene decomposed.	Methane found.	Calculated.	Variation.
		1 inch of heated tube.		
5 c.c.	80·10	43·72	53·40	−9·68
15 ,,	70·83	38·02	47·22	−9·20
40 ,,	50·58	25·12	33·72	−8·60
		6 inches of heated tube.		
5 c.c.	85·48	63·42	56·98	+6·44
15 ,,	79·42	44·44	52·94	−8·50
40 ,,	63·17	39·16	42·12	+2·96
		18 inches of heated tube.		
5 c.c.	93·76	70·13	64·50	+5·63
15 ,,	90·31	60·46	60·20	+0·26
40 ,,	87·15	55·37	58·10	−2·73

The fact that when only 1 in. of tube is heated there is a fairly constant deficit of the kind to be expected at the temperature employed, and that when a greater length of heated tube is used with a 5 c.c. rate of flow, the deficit becomes a substantial surplus, at once suggests that methane is amongst the secondary as well as the primary products of decomposition.

In the dilution experiments, the larger contraction in the volume noticeable points to the diluting of the products favouring polymerisation.

Dilution.	Ethylene decomposed.	Methane.		Variation.
		Found.	Calculated.	
Nil	72·27	40·85	48·18	−7·33
10 per cent ..	66·84	35·27	44·56	−9·29
25 ,, ..	53·85	33·43	35·90	−2·47
50 ,, ..	34·88	23·04	23·24	−0·20
75 ,, ..	15·15	13·43	10·10	+3·33
95 ,, ..	2·89	4·85	1·92	+2·93

And it seems probable from the figures that when dilution reaches above 50 per cent, not only is decomposition of the methane retarded, but formation as a secondary product commences.

Ever since water gas has been in use it has been well known that it contained traces of methane and acetylene, under conditions which render it impossible for them to have been formed from hydrocarbons remaining in the incandescent fuel, and the probabilities are that they have been produced, the acetylene by direct combination of carbon and hydrogen, and the methane by its partial decomposition.

The formation of ethylene from nascent hydrogen and acetylene takes place at such temperatures as those employed, and the amount so formed and again broken up by the radiant heat is purely a function of mass; so that I conceive from these experiments, the ethylene at once to a great extent decomposes under the influence of sufficiently high radiant heat according to the equation—

$$3C_2H_4 = 2C_2H_2+2CH_4,$$

and that the acetylene partly decomposes, the nascent hydrogen again uniting with more acetylene to reproduce ethylene, whilst other portions of the acetylene polymerise to benzene and other more complex hydrocarbons, and that, if the flow of this mixture be continued through a heated chamber, the action continues, the amount of ethylene regenerated becoming less and less, until it ceases to exist as a product of the decomposition.

It is well known that hydrogen will diffuse through ignited platinum into a vacuous space or even into other gases, and although no change in volume was observed when a mixture of 95 per cent hydrogen and 5 per cent ethylene was passed through the tube heated to 900° C.,

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* A Paper read before the Royal Society.

it seemed advisable to make special experiments to ascertain if any loss of hydrogen from this cause did take place at the temperature employed.

The apparatus having been fitted up as before, 6 in. of the tube were heated to between 900° and 1000° C., and a carefully measured volume of pure hydrogen was made to pass through it three times at a slow rate of flow, with the result that, after being brought back to its original temperature and pressure, it measured 99·5 per cent of the volume taken, showing that error from this cause is not likely to have taken place.

A new series of experiments was now undertaken to ascertain, if possible, how increase of contact with the heated walls of the containing vessel affected the amount and character of the decomposition taking place.

In order to do this, a small platinum tube, 2·5 m.m. in diameter and 45·72 c.m. long was taken in place of the one used in the previous experiments, which was 14 m.m. in diameter. The area of the big tube therefore, as compared with the area of the small tube, was as 1·54 to 0·049, and in order to obtain the relative amount of decomposition it is manifest that the rate of flow must be the same in both tubes.

If the rate of flow in the big tube be 40 c.c. per minute, then—

$$\frac{2{\cdot}5^2 \times 40}{14^2} = 1{\cdot}27$$

will give the required rate for the small tube.

Table V.

Temperature, 900° C. Rate of Flow, 1·27 c.c. per min.

Length of tube heated.	1 inch.		6 inches.		12 inches.	
Volume of gas—						
Before heating..	100		100		100	
After heating ..	80		91		97	
Analysis of Gaseous Products.						
Carbon dioxide ..	1·00		0·75		0·75	
Oxygen	0·25		0·00		0·25	
*Unsaturated hydrocarbons ..	15·30		12·20		6·30	
Carbon monoxide	0·75		1·00		1·00	
Saturated hydrocarbs. by absorp.	13·50	50·50	12·10	60·30	9·50	54·50
Do. by explos.	37·00		48·20		45·00	
Hydrogen	26·00		18·75		30·80	
Nitrogen	6·20		7·00		6·40	
*Containing acetylene	0·3		0·32		0·20	

Correcting the unsaturated hydrocarbons for change in volume, we obtain undecomposed—

I.	II.	III.
12·00	10·81	5·92

The ethylene used contained 96·75 per cent of unsaturated hydrocarbons; therefore the amount decomposed is—

I.	II.	III.
84·75	85·94	90·83

Turning now to the experiments made with the large tube and 40 c.c. a minute rate of flow, we find that the percentage of ethylene decomposed was—

I. 1 inch.	II. 6 inches.	III. 12 inches.
50·58	63·17	75·16 calcd.

an increase of decomposition with the small tube amounting to the following percentages:—

I.	II.	III.
33·93	22·48	15·48

showing that the maximum increase of 34 per cent rapidly falls with increased length of flow, whilst the ratio of area of heated surface to the passing gas is 43·96/7·85, or 5·6 times as great in the small tube as in the large, yet only gives an increase of one-third at most in the decomposition.

From the results of these experiments it may be stated that—

1. The initial decomposition of ethylene by heat is very rapid, and requires but a short flow through a heated containing vessel, such primary decomposition, however, being but slowly completed, owing to secondary reactions, which tend to reform ethylene.
2. Dilution has but little effect in retarding the decomposition of ethylene, unless it be very large.
3. Increase in rate of flow diminishes the amount of decomposition when the heated area is small, but rapidly diminishes in effect as the length of flow through a heated area increases.
4. The decomposition of ethylene is chiefly caused by radiant heat, the effect of which is very great as compared with the decomposition due to contact with heated surfaces.

I desire to acknowledge the valuable aid given me by Mr. F. B. Grundy in this investigation.

ARGON.*

By the Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D., F.R.S., Professor of Natural Philosophy, R.I.

It is some three or four years since I had the honour of lecturing here one Friday evening upon the densities of oxygen and hydrogen gases, and upon the conclusions that might be drawn from the results. It is not necessary, therefore, that I should trouble you to-night with any detail as to the method by which gases can be accurately weighed. I must take that as known, merely mentioning that it is substantially the same as is used by all investigators nowadays, and introduced more than fifty years ago by Regnault. It was not until after that lecture that I turned my attention to nitrogen; and in the first instance I employed a method of preparing the gas which originated with Mr. Vernon Harcourt, of Oxford. In this method the oxygen of ordinary atmospheric air is got rid of with the aid of ammonia. Air is bubbled through liquid ammonia, and then passed through a red-hot tube. In its passage the oxygen of the air combines with the hydrogen of the ammonia, all the oxygen being in that way burnt up and converted into water. The excess of ammonia is subsequently absorbed with acid, and the water by ordinary desiccating agents. That method is very convenient; and, when I had obtained a few concordant results by means of it, I thought that the work was complete, and that the weight of nitrogen was satisfactorily determined. But then I reflected that it is always advisable to employ more than one method, and that the method that I had used—Mr. Vernon Harcourt's method—was not that which had been used by any of those who had preceded me in weighing nitrogen. The usual method consists in absorbing the oxygen of air by means of red-hot copper; and I thought that I ought at least to give that method a trial, fully expecting to obtain forthwith a value in harmony with that already afforded by the ammonia method. The result, however, proved otherwise. The gas obtained by the copper method, as I may call it, proved to be one-thousandth part heavier than that obtained by the ammonia method; and, on repetition, that difference was only brought out more clearly. This was about three years ago. Then, in order, if possible, to get further light upon a discrepancy which puzzled me very much, and which, at that time, I regarded only with disgust and impatience, I published a letter in *Nature* inviting criticisms from chemists who

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* A Lecture delivered at the Royal Institution of Great Britain Friday, April 5, 1895.

might be interested in such questions. I obtained various useful suggestions, but none going to the root of the matter. Several persons who wrote to me privately were inclined to think that the explanation was to be sought in a partial dissociation of the nitrogen derived from ammonia. For, before going further, I ought to explain that, in the nitrogen obtained by the ammonia method, some—about a seventh part—is derived from the ammonia, the larger part, however, being derived as usual from the atmosphere. If the chemically-derived nitrogen were partly dissociated into its component atoms, then the lightness of the gas so prepared would be explained.

The next step in the enquiry was, if possible, to exaggerate the discrepancy. One's instinct at first is to try to get rid of a discrepancy; but I believe that experience shows such an endeavour to be a mistake. What one ought to do is to magnify a small discrepancy with a view to finding out the explanation; and, as it appeared in the present case that the root of the discrepancy lay in the fact that part of the nitrogen prepared by the ammonia method was nitrogen out of ammonia, although the greater part remained of common origin in both cases, the application of the principle suggested a trial of the weight of nitrogen obtained wholly from ammonia. This could easily be done by substituting pure oxygen for atmospheric air in the ammonia method, so that the whole, instead of only a part, of the nitrogen collected should be derived from the ammonia itself. The discrepancy was at once magnified some five times. The nitrogen so obtained from ammonia proved to be about one-half per cent lighter than nitrogen obtained in the ordinary way from the atmosphere, and which I may call for brevity "atmospheric" nitrogen.

That result stood out pretty sharply from the first; but it was necessary to confirm it by comparison with nitrogen chemically derived in other ways. The table before you gives a summary of such results, the numbers being the weights in grms. actually contained under standard conditions in the globe employed:—

Atmospheric Nitrogen.

By hot copper (1892)	2·3103
By hot iron (1893)	2·3100
By ferrous hydrate (1894)	2·3102
Mean	2·3102

Chemical Nitrogen.

From nitric oxide	2·3001
From nitrous oxide	2·2990
From ammonium nitrite purified at a red-heat	2·2987
From urea	2·2985
From ammonium nitrite purified in the cold	2·2987
Mean	2·2990

The difference is about 11 m.grms., or about one-half per cent; and it was sufficient to prove conclusively that the two kinds of nitrogen—the chemically-derived nitrogen and the atmospheric nitrogen—differed in weight, and therefore, of course, in quality, for some reason hitherto unknown.

I need not spend time in explaining the various precautions that were necessary in order to establish surely that conclusion. One had to be on one's guard against impurities, especially against the presence of hydrogen, which might seriously lighten any gas in which it was contained. I believe, however, that the precautions taken were sufficient to exclude all questions of that sort, and the result, which I published about this time last year, stood sharply out, that the nitrogen obtained from chemical sources was different from the nitrogen obtained from the air.

Well, that difference, admitting it to be established, was sufficient to show that some hitherto unknown gas is involved in the matter. It might be that the new gas was dissociated nitrogen, contained in that which was too light, the chemical nitrogen,—and at first that was the explanation to which I leaned; but certain experiments went a long way to discourage such a supposition. In the first place, chemical evidence—and in this matter I am greatly dependent upon the kindness of chemical friends—tends to show that, even if ordinary nitrogen could be dissociated at all into its component atoms, such atoms would not be likely to enjoy any very long-contiuued existence. Even ozone goes slowly back to the more normal state of oxygen; and it was thought that dissociated nitrogen would have even a greater tendency to revert to the normal condition. The experiment suggested by that remark was as follows:—to keep chemical nitrogen—the too light nitrogen which might be supposed to contain dissociated molecules—for a good while, and to examine whether it changed in density. Of course it would be useless to shut up gas in a globe and weigh it, and then, after an interval, to weigh it again, for there would be no opportunity for any change of weight to occur, even although the gas within the globe had undergone some chemical alteration. It is necessary to re-establish the standard conditions of temperature and pressure which are always understood when we speak of filling a globe with gas, for I need hardly say that filling a globe with gas is but a figure of speech. Everything depends upon the temperature and pressure at which you work. However, that obvious point being borne in mind, it was proved by experiment that the gas did not change in weight by standing for eight months—a result tending to show that the abnormal lightness was not the consequence of dissociation.

Further experiments were tried upon the action of the silent electric discharge,—both upon the atmospheric nitrogen and upon the chemically-derived nitrogen, but neither of them seemed to be sensibly affected by such treatment; so that, altogether, the balance of evidence seemed to incline against the hypothesis of abnormal lightness in the chemically-derived nitrogen being due to dissociation, and to suggest strongly, as almost the only possible alternative, that there must be in atmospheric nitrogen some constituent heavier than true nitrogen.

At that point the question arose, What was the evidence that all the so-called nitrogen of the atmosphere was of one quality? And I remember—I think it was about this time last year, or a little earlier—putting the question to my colleague, Professor Dewar. His answer was that he doubted whether anything material had been done upon the matter since the time of Cavendish, and that I had better refer to Cavendish's original paper. That advice I quickly followed, and I was rather surprised to find that Cavendish had himself put this question quite as sharply as I could put it. Translated from the old-fashioned phraseology connected with the theory of phlogiston, his question was whether the inert ingredient of the air is really all of one kind; whether all the nitrogen of the air is really the same as the nitrogen of nitre. Cavendish not only asked himself this question, but he endeavoured to answer it by an appeal to experiment.

I should like to show you Cavendish's experiment in something like its original form. He inverted a U-tube filled with mercury, the legs standing in two separate mercury cups. He then passed up, so as to stand above the mercury, a mixture of nitrogen, or of air, and oxygen; and he caused an electric current from a frictional electrical machine, like the one I have before me, to pass from the mercury in the one leg to the mercury in the other, giving sparks across the intervening column of air. I do not propose to use a frictional machine to-night, but I will substitute for it one giving electricity of the same quality of the construction introduced by Mr. Wimshurst, of which we have a fine specimen in the Institution. It stands just outside the door of the theatre, and will supply an electric current along insulated wires, leading to the mercury cups; and, if we are successful, we shall cause sparks to pass through the small length of air included above the columns of mercury. There they are; and after a little time you will notice that the mercury rises, indicating that the gas is sensibly absorbed under the influence of the sparks and of a piece of potash floating on the mercury. It was by that means that Cavendish established his great discovery of the nature of the inert ingredient in the atmosphere, which we now call nitrogen; and, as I have said, Cavendish himself proposed the question, as distinctly as we can do, Is this inert ingredient all of one kind? and he proceeded to test that question. He found, after days and weeks of protracted experiment, that, for the most part, the nitrogen of the atmosphere was absorbed in this manner, and converted into nitrous acid; but that there was a small residue remaining after prolonged treatment with sparks, and a final absorption of the residual oxygen. That residue amounted to about $\frac{1}{120}$th part of the nitrogen taken; and Cavendish draws the conclusion that, if there be more than one inert ingredient in the atmosphere, at any rate the second ingredient is not contained to a greater extent than $\frac{1}{120}$th part.

I must not wait too long over the experiment. Mr. Gordon tells me that a certain amount of contraction has already occurred; and if we project the U upon the screen, we shall be able to verify the fact. It is only a question of time for the greater part of the gas to be taken up, as we have proved by preliminary experiments.

In what I have to say from this point onwards, I must be understood as speaking as much on behalf of Professor Ramsay as for myself. At the first, the work which we did was to a certain extent independent. Afterwards we worked in concert, and all that we have published in our joint names must be regarded as being equally the work of both of us. But, of course, Professor Ramsay must not be held responsible for any chemical blunder into which I may stumble to-night.

By his work and by mine the heavier ingredient in atmospheric nitrogen which was the origin of the discrepancy in the densities has been isolated, and we have given it the name of "argon." For this purpose we may use the original method of Cavendish, with the advantages of modern appliances. We can procure more powerful electric sparks than any which Cavendish could command by the use of the ordinary Ruhmkorff coil stimulated by a battery of Grove cells; and it is possible so to obtain evidence of the existence of argon. The oxidation of nitrogen by that method goes on pretty quickly. If you put some ordinary air, or, better still, a mixture of air and oxygen, in a tube in which electric sparks are made to pass for a certain time, then in looking through the tube, you observe the well-known reddish orange fumes of the oxides of nitrogen. I will not take up time in going through the experiment, but will merely exhibit a tube already prepared (image on screen),

One can work more efficiently by employing the alternate currents from dynamo machines which are now at our command. In this Institution we have the advantage of a public supply; and if I pass alternate currents originating in Deptford through this Ruhmkorff coil, which acts as what is now called a "high potential transformer," and allow sparks from the secondary to pass in an inverted test-tube between platinum points, we shall be able to show in a comparatively short time a pretty rapid absorption of the gases. The electric current is led into the working chamber through bent glass tubes containing mercury, and provided at their inner extremities with platinum points. In this arrangement we avoid the risk, which would otherwise be serious, of a fracture just when we least desired it. I now start the sparks by switching on the Ruhmkorff to the alternate current supply; and, if you will take note of the level of the liquid representing the quantity of mixed gases included, I think you will see after, perhaps, a quarter of an hour that the liquid has very appreciably risen, owing to the union of the nitrogen and the oxygen gases under the influence of the electrical discharge, and subsequent absorption of the resulting compound by the alkaline liquid with which the gas space is enclosed.

By means of this little apparatus, which is very convenient for operations upon a moderate scale, such as for analyses of "nitrogen" for the amount of argon that it may contain, we are able to get an absorption of about 80 c.c. per hour, or about 4 inches along this test-tube, when all is going well. In order, however, to obtain the isolation of argon on any considerable scale by means of the oxygen method, we must employ an apparatus still more enlarged. The isolation of argon requires the removal of nitrogen, and, indeed, of very large quantities of nitrogen, for, as it appears, the proportion of argon contained in atmospheric nitrogen is only about 1 per cent, so that for every litre of argon that you wish to get you must eat up some hundred litres of nitrogen. That, however, can be done upon an adequate scale by calling to our aid the powerful electric discharge now obtainable by means of the alternate current supply and high potential transformers.

In what I have done upon this subject I have had the advantage of the advice of Mr. Crookes, who some years ago drew special attention to the electric discharge or flame, and showed that many of its properties depended on the fact that it had the power of causing, upon a very considerable scale, a combination of the nitrogen and the oxygen of the air in which it was made.

I had first thought of showing in the lecture-room the actual apparatus which I have employed for the concentration of argon; but the difficulty is that, as the apparatus has to be used, the working parts are almost invisible, and I came to the conclusion that it would really be more instructive as well as more convenient to show the parts isolated, a very little effort of imagination being then all that is required in order to reconstruct in the mind the actual arrangements employed.

First, as to the electric arc or flame itself. We have here a transformer made by Pike and Harris. It is not the one that I have used in practice; but it is convenient for certain purposes, and it can be connected by means of a switch with the alternate currents of 100 volts furnished by the Supply Company. The platinum terminals that you see here are modelled exactly upon the plan of those which have been employed in practice. I may say a word or two on the question of mounting. The terminals require to be very massive on account of the heat evolved. In this case they consist of platinum wire doubled upon itself six times. The platinums are continued by iron wires going through glass tubes, and attached at the ends to the copper leads. For better security, the tubes themselves are stopped at the lower ends with corks and charged with water, the advantage being that, when the whole arrangement is fitted by means of an indiarubber stopper into a closed vessel, you have a witness that, as long as the water remains in position, no leak can have occurred through the insulating tubes conveying the electrodes.

Now, if we switch on the current and approximate the points sufficiently, we get the electric flame. There you have it. It is, at present, showing a certain amount of soda. That in time would burn off. After the arc has once been struck, the platinums can be separated; and then you have two tongues of fire ascending almost independently of one another, but meeting above. Under the influence of such a flame, the oxygen and the nitrogen of the air combine at a reasonable rate, and in this way the nitrogen is got rid of. It is now only a question of boxing up the gas in a closed space, where the argon concentrated by the combustion of the nitrogen can be collected. But there are difficulties to be encountered here. One cannot well use anything but a glass vessel. There is hardly any metal available that will withstand the action of strong caustic alkali and of the nitrous fumes resulting from the flame. One is practically limited to glass. The glass vessel employed is a large flask with a single neck, about half full of caustic alkali. The electrodes are carried through the neck by means of an india-rubber bung provided also with tubes for leading in the gas. The electric flame is situated at a distance of only about half an inch above the caustic alkali. In that way an efficient circulation is established; the hot gases as they rise from the flame strike the top, and then as they come round again in the course of the circulation they pass sufficiently close to the caustic alkali to ensure an adequate removal of the nitrous fumes.

There is another point to be mentioned. It is necessary to keep the vessel cool; otherwise the heat would soon rise to such a point that there would be excessive generation of steam, and then the operation would come to a standstill. In order to meet this difficulty the upper part of the vessel is provided with a water-jacket, in which a circulation can be established. No doubt the glass is severely treated, but it seems to stand it in a fairly amiable manner.

By means of an arrangement of this kind, taking nearly three horse-power from the electric supply, it is possible to consume nitrogen at a reasonable rate. The transformers actually used are the "Hedgehog" transformers of Mr. Swinburne, intended to transform from 100 volts to 2400 volts. By Mr. Swinburne's advice I have used two such, the fine wires being in series so as to accumulate the electrical potential and the thick wires in parallel. The rate at which the mixed gases are absorbed is about 7 litres per hour; and the apparatus, when once fairly started, works very well as a rule, going for many hours without attention. At times the arc has a trick of going out, and it then requires to be re-started by approximating the platinums. We have already worked fourteen hours on end, and by the aid of one or two automatic appliances it would, I think, be possible to continue operations day and night.

The gases, air and oxygen in about equal proportions, are mixed in a large gasholder, and are fed in automatically as required. The argon gradually accumulates; and when it is desired to stop operations the supply of nitrogen is cut off, and only pure oxygen allowed admittance. In this way the remaining nitrogen is consumed, so that, finally, the working vessel is charged with a mixture of argon and oxygen only, from which the oxygen is removed by ordinary well-known chemical methods. I may mention that at the close of the operation, when the nitrogen is all gone, the arc changes its appearance, and becomes of a brilliant blue colour.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

THE CONVERSAZIONE AT THE ROYAL SOCIETY.

June 12th, 1895.

Among the articles exhibited and the procedures shown at this Converzazione there were not a few which must exceptionally appeal to readers of the Chemical News.

Thus, in Room No. 1 (the office) we noticed an electrograph for indelible linen marking. The linen is moistened with a saline solution, or in default with plain water, and a current is passed for about two minutes from a silver die, thus conveying silver into the fibres wherever the die touches. On reversing the current for three seconds, the silver thus deposited in the tissue is reduced, fixed in the metallic state. We believe that an analogous process has been successfully applied in certain styles in tissue-printing.

In Room 2 (the Reception Room) Dr. Gladstone, F.R.S., exhibited photographs of curvilinear crystals of water and specimens of curvilinear crystals of soda salts. The scientific importance of this exhibit is of great moment: it was formerly maintained that only organic bodies, *e.g.*, animals and plants or their parts, can solidify in curvilinear figures. The only familiar exception to this rule, the diamond, was explained as being pre-eminently *the* organic element.

In Room No. 3 (the Council Room), Mr. W. Gowland exhibited Japanese pictures as showing the effects of time on the pigments used by Japanese artists from A.D. 1322 to the beginning of the present century. For greens and blues these painters used copper carbonate; for a permanent blue, *Lapis lazuli*, *i.e.*, natural ultramarine. For reds, ferric oxide, vermilion, and carmine; for permanent white, levigated oyster shells; and for a black, a lamp-black from the oil of *Sesamum indicum*.

Prof. Roberts-Austen, C.B., F.R.S., exhibited the electrical furnace used for obtaining carbon in the diamond state and for fusing chromium, titanium, platinum, and others of the most refractory metals. The furnace has a fire-clay case lined with magnesia, and the crucibles used are of magnesia. The carbon poles lie horizontally, and the arc is deflected upon the material to be heated by means of a magnet. In exhibiting the process, an image of the melted contents of the furnace is thrown upon a screen by means of a lens and mirror. The current used was from 60 to 70 ampères and 100 volts. This exhibition was strikingly satisfactory.

In Room 4 (Principal Library), Mr. J. Norman Lockyer, C.B., F.R.S., showed photographs of apparatus used for collecting the gases obtained from various minerals by the distillatory method. The small retort containing the specimen is attached end-wise to a spectrum tube joined to a Sprengel pump. After exhaustion, the mineral is heated to redness and the spectra of the gases emitted at different stages are observed in the spectrum tube and photographed.

The same *savant* exhibits also photographs of the spectra of Bellatrix, and of a part of the sun's atmosphere. Here are seen coincidences with the lines as photographed in the spectra of the gases evolved from uraninite. It is remarked that "we appear to be in presence of the *vera causa* of many of the lines hitherto classed as unknown."

A further exhibition shows the spectra of the rare gases:—

(*a*) Presence of the yellow line D_3; in some cases with the blue line 4471, and in others without it.

(*b*) Presence of yellow line with the ultra-violet line 3889, and in other cases without it.

A set of experiments showing inversions in the intensities of lines appearing in the spectra of the new gas from uraninite.

In the same room, Mr. W. F. H. Blandford showed specimens illustrating chromogeny in South American butterflies, interesting both to the chemist and the biologist.

Mr. W. T. Burgess exhibited experiments demonstrating the conveyance of infection by flies. The part played by these insects in the diffusion of pathogenic microbia is now placed beyond all doubt.

Prof. Marshall Ward, F.R.S., exhibited a series of cultures of bacteria isolated from the water of the Thames. Some of these are still unknown.

The Marine Biological Association showed the method of fixing methylene-blue preparations by means of ammonium molybdate, as invented by Dr. Barthe, of Berlin.

Prof. A. Liversidge, F.R.S., exhibits sectioned of gold nuggets etched to show their crystalline structure. The designs brought out on slicing, polishing, and etching with chlorine-water resemble the well-known Widmanstatt figures, but are more or less square in section.

Prof. Ramsay, F.R.S., exhibited spectra of argon and of helium mixed with argon. A sodium flame is shown to prove the non-identity of the D_3 line of helium with the sodium D_1 and D_2 lines.

PHYSICAL SOCIETY.

Ordinary Meeting, June 14th, 1895.

Captain W. de W. Abney, President, in the Chair.

Mr. **Burstall** continued the reading of his paper "*On the Measurement of Cyclically varying Temperature.*"

Three sizes of platinum wire have been employed for the thermometers, in order that some idea might be formed as to the magnitude of the error caused by the lag of the temperature of the wire behind that of the gases. The constants of the platinum thermometers were determined either by comparison with a standard Callendar platinum thermometer, or by means of ice, boiling water, and boiling sulphur. In most cases the thermometer constants were determined after the wire had been exposed to the action of the hot gases for about half an hour. One wire, however, was calibrated before being used, and an unusually high value was obtained for the coefficient δ. After this wire had been exposed to the hot gases, the value of δ fell, however, to the normal. The author thinks the abnormal value may have been due to the formation of a gold-platinum alloy during the process of attaching the wire to the leads, and that this alloy was subsequently swept off by the hot gases.

The paper includes a number of tables and curves which embody the numerical results, and show that concordant results can be obtained on different days and with different thermometers.

Prof. **Perry** said that an instrument for quickly recording varying temperatures was greatly required by engineers. The temperature just inside the cylinder-walls was, however, most important to determine; and a knowledge of how the temperature from 1 to 2 m.m. inside the walls varied would be of the greatest value. He would like to ask the author if the observed temperatures agreed with the values calculated on the assumption that the gases in the cylinder behaved as a perfect gas, and that—

$$\frac{PV}{T} = \text{constant}$$

during the whole stroke. Differences between the observed and calculated values might be due to dissociation, and not entirely to lag in the thermometers. It was astonishing that even the fine wires employed were able to follow the rapidly varying temperature, and he would like to see some special experiments made to test this point.

Prof. **Capper** showed a diagram giving the values calculated on the assumption that—

$$\frac{PV}{T} = \text{constant.}$$

In such a calculation it was necessary to assume some temperature as a starting point, and in general this temperature was obtained from an analysis of the exhaust gases, so that the calculated curve is most likely to depart from the truth at the commencement of the stroke. He (Prof. Capper) hoped that the author would be able to accurately determine the temperature of some one point of the stroke, and he suggested that the point where the observed curve crossed the theoretical curve would be the most suitable one for this purpose. Such a point must exist, since at the commencement of the stroke the lag causes the observed temperature to be too low, while at the end of the stroke the observed temperatures are too high. Mr. Burstall finds a curious bump in his curves, and it is curious that a similar bump exists in the calculated curves. From the constancy with which this bump appears, it would seem that it must have some physical meaning. It was important to remember that the expansion of the gas-engine cylinder is not adiabatic, for heat is both abstracted and generated during the stroke.

Mr. **Blakesley** suggested that since the temperatures dealt with were sufficient to make the wire red-hot, the question of lag might be investigated by means of Becquerel's phosphoroscope at a known interval after the removal of the source of heat.

Mr. **Griffiths** said he considered an important source of error was the large thermal capacity of the leads when the working wire was so very short. He thought it would be possible to standardise the thermometers under conditions somewhat similar to those which occur in the engine cylinder. Thus, perhaps alternate gushes of air at 0° and 100° C. might be used. The use of gold to attach the fine wire to the leads was objectionable, since the gold must permeate the platinum for quite an appreciable fraction of the whole length of the wire. He would like to know whether the change in δ alluded to by the author occurred with the first explosion or whether it was a gradual one.

Mr. **Enright** pointed out that the nature of the working substance in a gas-engine varied during the stroke.

Prof. **Perry** said that the change in the specific volume of the gases before and after combustion did not amount to more than 1·25 per cent.

Mr. E. **Wilson** said he thought it was most important to shorten the time of contact, since at present the galvanometer readings corresponded to the mean temperature over a range of about 5 per cent of the whole stroke. It might be possible to make use of a condenser to get over this difficulty.

Prof. **Rücker** said that the Kew Observatory were making arrangements to undertake the testing of platinum thermometers.

Mr. **Enright** suggested that with a very short contact induced currents might cause errors.

Mr. **Rhodes** said that he had found that the method of determining the zero-point of thermometers, by means of melting ice, was far from satisfactory, and that the results obtained could not be depended upon to within 0·1° C.

The author, in his reply, said the only chemical action on the wires he thought probable was the formation of a carbide. After several hours use, however, the wires appear quite bright and clean.

Mr. N. F. **Deerr** read a paper on "*The Thermal Constants of the Elements.*"

The object of the paper is to establish the following laws:—If T denote the melting-point on the absolute scale, C the mean coefficient of expansion between zero and the melting-point, S the mean specific heat, and L the latent heat of fusion, then, for any family in Mendeleeff's periodic classification, the following relations will hold between metals and metals, and between non-metals and non-metals:—

$$\left(T + \frac{L}{S}\right) C = \text{const.}$$

$$TC = \text{const.}$$

$$\frac{LC}{S} = \text{const.}$$

In the absence of other data the mean values of C and S between 0° and 100° have been taken.

Anomalous values are obtained in the case of gold and mercury, if these metals are included in their usual positions. The author considers that the thermal constants indicate that gold ought to be placed among the transition elements. He further proposes to place mercury in a new group to come before the lithium group. Such a group, he suggests, would at present contain hydrogen, argon, and mercury.

The paper concludes with an attempt to justify the expression—

$$\left(T + \frac{L}{S}\right) C = \text{const.}$$

on theoretical grounds.

Dr. **Gladstone** considered that the paper contained valuable numerical relationships, and that the second and third formulæ were much more strongly supported by the data given than the first formula. He, the speaker, had also previously noticed that the elements of the transition group might be subdivided into sub-groups, and that the elements of each of these sub-groups were particularly closely related. He agreed with the author that gold ought not to be included in the first group.

Mr. F. H. **Neville** said that since the author did not give the source of the data he had employed, most of the results given were rather indefinite. For example, while the author gives 870° as the melting-point of aluminium, Mr. Haycock and himself had found the value 927°. The value of the latent heat of aluminium given was 29·3, while Pionchon, in a recent paper in the *Comptes Rendus*, gives the value 80. Theoretical considerations appear to indicate that 80 is the minimum value possible. The author assumes that when you heat a substance from the absolute zero to its melting-point, all the energy supplied is employed in the work of expansion. Some of the heat, however, must be employed in changing the kinetic energy of the molecules, even in the case of a solid.

Prof. **Worthington** said that in some cases the amount of work done against cohesive forces between 0° and 100° was much less than one ten-thousandth of the whole amount of energy supplied.

Mr. **Griffiths** said he did not believe in any generalisation which depended on the values of the specific heats determined between 0° and 100°, the rate of change with temperature of specific heat being so great.

The author, in his reply, said he had made every endeavour to obtain the most accurate data for his calculations. The value 29·3 for the latent heat of aluminium was obtained from a paper by J. G. Richards.

A paper on "An Electromagnetic Effect," by Mr. F. W. Bowden, was postponed till the next meeting.

NOTICES OF BOOKS.

Chemical Technology, or Chemistry in its Applications to Arts and Manufactures. Edited by C. E. Groves, F.R.S., and W. Thorp, B.Sc. With which is incorporated "Richardson and Watt's Chemical Technology," Vol. II., Lighting. 8vo. London: J. and A. Churchill. 1895.

The work before us, if calculated to be very bulky, gives no less a promise of high value or unquestionable excellence. Its successive sections are devoted respectively to fats and oils, by W. Y. Dort; the stearine industry, by J. McArthur; the candle manufacture, by J. and F. A. Field; the petroleum industry and lamps, by Boverton Redwood; and miners' safety-lamps, by B. Redwood and D. A. Louis. No small part of the volume, it will be perceived, treats of matter which pertains to mechanical technology, *i. e.*, the construction of lamps, both for ordinary purposes and for miners' safety-lamps.

In the Introduction we find some hints which may save inventors from mistakes. Thus we are reminded that a room which would be well lighted by means of twenty candles, will be but poorly lighted by means of a single lamp giving light equal to twenty candles. Further, if the flame of such a lamp be surrounded by an opal globe it will be found that the room is better lighted than by the naked flame, though in all probability the globe will intercept one-half of the light.

In the second chapter the delicate question of ascertaining the purity of fats and oils is discussed at considerable length. The after-taste left by mineral and rosin oils at the back of the throat is correctly pronounced a delicate test for such oils.

Maumené's temperature reaction is pronounced valuable in many cases, though, according to Moschini, a previous exposure of the sample to sunlight interferes with the test as far as olive oil is concerned.

The colour-reactions, which were very carefully studied by Calvert and by Chateau, are now considered as o doubtful value, since the reaction, leaving adulterants out of the question, may depend on substances which naturally accompany the oils. They are also modified by the age and condition of the samples, the soil and the climate where they have been produced, and by the degree and method of refining.

The so-called cohesion figures may lead to useful results if the observer has sufficient experience, and if he has at hand pure specimens for comparison.

The absorption spectra enable us to distinguish vegetable oils from those of animal origin. But a very thorough refining is apt to destroy the chlorophyll on which the bands depend.

The use of mineral and rosin oils as adulterants may often be detected by determining the proportion of non-saponifiable oil in the sample.

It is stated that 300,000 tons of Egyptian cotton-seed are now yearly crushed in Britain. It is very satisfactory to learn that the cultivation of the olive is carried on with success in Queensland and South Australia. Of all oils that obtained from olives is most shamelessly sophisticated; some samples sold as fine salad oil are now cotton oil pure and simple.

We do not find here any mention of the new process for obtaining from the cocoa-nut a fatty matter which is probably the best substitute for butter.

Cod-liver oil does not appear to be mentioned, though there is a passing note of its occasional "surrogate," shark-liver oil.

The manufacture of stearine is carefully expounded by J. McArthur, with an account of the three methods of decomposing the neutral fats, viz., saponification with lime or some other base, and decomposition with water alone and with sulphuric acid. The two latter processes are commonly spoken of as saponification.

The candle manufacture is shown by L. and F. A. Field. It is somewhat surprising that, in the very face of the electric light, of gas, and of petroleum lamps, the candle still holds its own. The reason is doubtless its superior simplicity, its convenience, and portability. Nor does it sin so grossly against economy as it is sometimes assumed, since by its means light is obtained where, and only where, it is wanted, whilst gas and the electric light expend much of their energy on the ceiling.

The very rush-light, of course home-made, still sheds its feeble rays in rustic cottages, where at any rate it does not cause explosions.

The night-light is a cheap and useful device of recent times, and is the more to be commended because the fumes of a petroleum lamp when turned down to a mere speck are very anti-sanitary.

The fourth section, on the petroleum industry, by Boverton Redwood, may, both from its extent and its elaborate character, claim the rank of a monograph. We have the history of the mineral oils from a remote antiquity; of the development of petroleum and natural gas industry in the United States, in Russia, in Canada, and in Galicia, as well as in deposits of less importance, including the Assam and Burmese oil-fields.

The geology of petroleum and its origin are next discussed. Mr. Redwood seems disinclined to favour the views of Prof. Mendeleeff; but considers, with Lesley, that the whole mass of animal and vegetable matter in the earth is in the course of successive conversion into light oils, heavy oils, asphalte, and albertite, these changes being accompanied with the liberation of gaseous hydrocarbons.

Incidentally there is a mention of the unfortunate Torbane Hill litigation,—a deplorable affair, since it gave occasion to the enemies of Science to blaspheme. It appears that there exists in New South Wales a deposit resembling in its properties and uses the Scottish Torbane Hill mineral.

Space does not permit us to notice the elaborate account of safety-lamps for mining purposes. One little point, concerning locking and unlocking safety-lamps, we must venture to notice: the motive of the miner for unlocking his lamp is not the desire of obtaining a little more light, but to light his pipe!

It appears that Vol. iii., announced as nearly ready, will also be devoted to means of artificial illumination. The whole work promises, when complete, to be an invaluable library of reference.

CORRESPONDENCE.

THE MOST PROBABLE ATOMIC WEIGHT OF YTTRIUM.

To the Editor of the Chemical News.

SIR,—Since you have kindly reprinted my paper on the atomic weight of yttrium (*Am. Chem. Journ.*, xvii., 154; CHEMICAL NEWS, vol. lxxi., p. 155), I would ask for a little space in your journal to add a word to the letter of Mr. Delafontaine which has appeared on this subject (CHEMICAL NEWS, vol. lxxi., p. 243).

In reference to the historical omissions, it must be said that I have duly cited the work of Mr. Delafontaine, as calculated by Meyer and Seubert in the "Atomgewichte der Elemente" for 1865, and also for 1866.

The determinations of Berlin are quoted neither by Meyer and Seubert, nor by Ostwald in his "Lehrbuch." The original paper of Berlin is not accessible to me, but an abstract (*Berichte*, vi., 1468) states that he found exactly the same value as Clève and Höglund, which, as calculated to-day, is 89·58.

The statement of Mendeleeff in his "Principles of Chemistry" (Translation, p. 88), which gives neither the method of purifying his yttria, nor the method of making the determinations, nor the separate results, can hardly be accepted as the most trustworthy account of the determination of the atomic weight of yttrium; indeed, it is not even referred to by either of the authorities on atomic weights above mentioned.

Coming, now, to the main point—Why has Clève's result been accepted as the most probable? Mr. Delafontaine thinks it is due to Clève's reputation, and because his result fits in with the Periodic System. In matters pertaining to the rarer elements, Clève is indeed a high authority, but what seems to me to be of more importance, is the fact that Clève has worked subsequent to Delafontaine and many others in this field, and has had the benefit of their experience as well as of his own.

The second reason offered does not seem to be very forcible, since chemists are surely not wedded to such an extent to a system in which the inconsistencies are occasionally as striking as the agreements.

Clève's value, as given in Mr. Delafontaine's paper, is 89·7, and it is stated that his yttria was pale yellow. Mr. Delafontaine does not give references to the literature, so that it is difficult to determine just what papers he has in mind. From the latest determinations of Clève (*Bull. Soc. Chim.*, xxxix., 120) it is stated that 23·2091 grms. of yttrium sulphate gave 11·2568 grms. of the oxide, from which, when O = 16 and S = 32·06, yttrium = 89·1. Again, I find no authority for the statement that Clève's yttria was yellow; he claims that the yttria used in his last work was pure, and adds:—"L'yttria pure est parfaitement blanche sans trace de teinte jaune."

It is to be regretted that Mr. Delafontaine does not tell us *why* Clève's results are wrong, rather than end the matter with the statement that they are "evidently inaccurate." It seems to me that the work of Clève has been accepted because it bears internal evidence of its own worth, and not alone for the reasons stated by Mr. Delafontaine. My own results, from yttria purified by Prof. Rowland, leads also to the conclusion that Clève's results are only a little too high.—I am, &c.,

HARRY C. JONES.

Chemical Laboratory,
Johns Hopkins University,
June 4, 1895.

REMOVAL OF STOPPERS BY ELECTRICITY.

To the Editor of the Chemical News.

SIR,—Every chemist has experienced the difficulty of removing the glass stopper of a bottle when it has become fixed, apparently immovably. Of course, the best remedy is to heat the neck of the bottle for awhile over a Bunsen burner; the serious drawback, however, of this old-fashioned method lies in the fact that the bottle must be held in horizontal position, and the fluid or solution may be easily spilled out of the bottle if the operation is performed carelessly.

I have solved this little problem in an efficacious, up-to-date, though expensive, manner by rigging up an adjustable clamp with coils of platinum wires embedded in a strip of asbestos attached to the clamp. You press the circular clamp round the neck of the glass bottle, then "press the button, and electricity does the rest."—I am, &c.,

R. W. HILL.

Manchester.

NOTE ON THE

ESTIMATION OF TOTAL ALKALI IN SOAP.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS (vol. lxxi., p. 285) I have noticed the above inserted as an article of original work by Mr. J. A. Wilson. I cannot see where the originality comes in; he tells us the "determination by difference of free alkali in soap solutions is unreliable, and that he has given up direct titration," at the same time illustrating his remarks in the above note by giving some examples which are only clear to himself.

I should think it would be more interesting if he gave us a new reliable method instead of pointing out errors which are already known. It is all very well to find fault with methods if one can improve them, otherwise it is useless criticising them.—I am, &c.,

P. L. ASLANOGLOU.

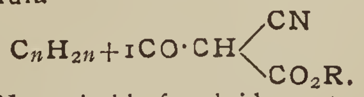
CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 22, June 4, 1895.

Volume of Salts in their Aqueous Solutions.—Lecoq de Boisbaudran.—The author holds that it is sometimes advantageous to measure changes of volume by effecting the solution in a dilatometer—an apparatus full of liquids fitted with a graduated stem on which the absolute values of the charges are read off.

Melthenic and Methinic Acids.—A Contribution to the Study of the Acetyl-cyanacetic Ethers of the General Formula—



$$C_nH_{2n+1}CO{\cdot}CH\langle{}^{CN}_{CO_2R}.$$

—A. Haller.—Not suitable for abridgment.

The Specific Gravity of Helium.—Prof. Clève.—Inserted in full.

The Reduction of Nitrous Oxide by Metals in Presence of Water.—Paul Sabatier and J. B. Senderens.

—The results of the authors prove that nitrous oxide in solution is reduced to the state of nitrogen by magnesium, zinc, iron, and even cadmium, with the simultaneous formation of a little ammonia. The gas, on contact with metals moistened with water, dissolves gradually in this water, and is finally reduced in the same manner.

Formation Heat of Sodium Acetylene.—De Forcrand.—The author's results, taking diamond as the form of carbon, appears to be $-9{\cdot}76$ cal., whilst for calcium acetylide it was $-2{\cdot}96$ cal.

On Phthalyl Chloride and Phthalide.—Paul Rivals.

A Thermo-chemical Investigation.—Conductivity of Certain β-Ketonic Ethers.—J. Guinchant.—The sodium salts of the cyanomethinic acids behave, as concerns their conductivity, in an absolutely normal manner. These acids, like acetyl acetone, obey Ostwald's law ($K = \text{const.}$) as far as it could be expected from compounds containing an acid group and an ether function. For many of these compounds the neutralisation-heat has already been determined, and their chemical affinity deduced from the thermo-chemical measurements agrees with that inferred from the conductivities. For the homologous acids the values of K decrease in proportion as the molecular weight rises.

Determination of Volatile Acids in Wines.—E. Burcker.—The author has found experimentally that the fixed acids, free or combined, exert at most only a negligible action upon the acidity of the distillate, which is due merely to the volatile acids among which the acetic acid takes the principal work. The maximum limit of volatile acidity in sound French wines does not exceed 0·70 grm. per litre, calculated as SO_4H_2. For the wines of Algeria and Tunis it may rise to 1·60 grm. per litre.

Oidium albicans a General Pathogenic Agent.—MM. Chanin and Ostrowsky.—This paper is mainly of medical importance, but it shows that the *Oidium albicans* is a pathogenic agent to be kept in view in sanitary observations. (See Prof. Lehmann, "Methods of Practical Hygiene," translated by W. Crookes, F.R.S., vol. i., p. 159.)

Bulletin de la Société Chimique de Paris.
Series 3, Vols. xiii.-xiv., No. 5, 1895.

On Natural Dioxystearic Acid.—Paul Juillard.—On saponifying castor oil with caustic soda, the author obtained an isolated or new acid, $C_{18}H_{36}O_4$, an isomer of the acid which he had formerly obtained in alizarene red oils. The acid is insoluble in ether, ligroine, and benzene, scarcely soluble in cold toluene, but more freely if hot; soluble in boiling alcohol and acetic acid. It melts at 141° to 143°. It is a saturated acid of the series $C_nH_{2n}O_4$. It contains two hydroxyls of an alcoholic character, which renders them capable of condensation. According to the manner of treatment it forms two classes of distinct products.

On Triricinoleine, its Ethers and its Synthesis. Artificial Castor Oil.—Paul Juillard.—This synthesis has been effected by heating ricinic acid with glycerin, keeping closely within certain limits of temperature.

On the Constitution of Iodine Green.—Léon Lefèvre.—The iodine green of Hofmann and Girard is an iodomethylate of tetramethyl-triaminodiphenyl cresylmethanol, and not of hexamethyl-triaminodiphenyl cresylmethanol, as certain German *savants* have admitted without proof and without regard to the analysis of Hofmann and Girard. If heated it loses CH_3I, and gives a violet of tetramethyl-triamino-diphenyl cresylmethanol.

Researches on Pectase, and on the Pectic Fermentation.—G. Bertrand and A. Mallèvre.—The authors conclude that pectase exists in solution as well in the cellular juice of acid fruits as in that of the roots of carrots. There is no insoluble pectase.

MEETINGS FOR THE WEEK.

Tuesday, 25th.—Photographic, 8.
Wednesday, 26th.—Society of Arts, 4. (Anniversary).
—— British Astronomical Association, 5.
Thursday, 27th.—Royal Society Club, 6.30. (Anniversary).
Friday, 28th.—Physical, 5. "An Electromagnetic Effect," by F. W. Bowden. "On Synchronous Motors," by W. G. Rhodes. "The Electrical Properties of Selenium," by Shelford Bidwell, F.R.S.

THE CHEMICAL NEWS.

VOL. LXXI., No. 1857.

ON THE NEW SYSTEM OF CASTING CRUCIBLE STEEL INGOTS FOR TOOL MANUFACTURE.

By SERGIUS KERN, M.E., St. Petersburg.

IN the CHEMICAL NEWS (vol. lxxi., pp. 187 and 220) some details were inserted concerning our proposed system of casting crucible steel ingots, used for forging various *tools*, not *bars*, for the market, as they would be in the majority of cases too short.

We cast now for trials, at the small steel-foundry of the New Admiralty, St. Petersburg, six flat ingots, which have a remarkably sound appearance (about 9″×9″; height, 3½ inches; weight, ⅔ cwt.).

On the surface is found a small cup-form piping, which is very shallow. In order to have the stream of steel, to go right into the middle of the mould, we used a burnt clay tumbler, ordinarily placed into the bottom of Siemens-Martin casting ladles, and 1½ inches diameter at the lower end. This tumbler is supported over the mould by the means of an iron ring with cross-bars.

The ready-melted steel is poured into an empty crucible heated to redness, containing 30 grms. of metallic aluminium, and from here into the first crucible again, and finally through the tumbler into the mould. The steel is covered with a lid 2″ thick, and pulverised glass is thrown on its sides. The mould stands on a burnt clay smooth plate, and is slightly brushed inside with previously boiled gas-tar. The flat ingot produced is cleaned superficially by chiselling from the small cracks, &c.

In a short time I will send a report of the *modus operandi* of forging such ingots, the method of which was shortly mentioned in our notes in the above-named pages of the CHEMICAL NEWS. There is no nuisance at all if the cup-form piping happens to be somewhere near one of the corners of the square; the method of cutting the ingots under steam-hammer must only be slightly altered.

THE PRACTICAL WORKING OF PELOUZE'S PROCESS.

By VINCENT EDWARDS, F.C.S.

As manures sometimes contain nitrates of soda and potash, the latter salt especially being added when a concentrated mixture is required for garden purposes, the following notes may be useful to works chemists and others who wish to estimate rapidly the amount of nitric nitrogen, and have found this method as usually described troublesome and inaccurate:—

I use a 600 c.c. glass flask, with a good rubber stopper, fitted with a tube and a Bunsen valve, the opening in which is made with a razor, which is more satisfactory than a knife; as much depends upon the working of the valve, it is well to ascertain before commencing that it behaves correctly. The following solutions are required:—(1), 100 grms. crystallised sulphate of iron and 100 c.c. strong H_2SO_4, made up with water to 1 litre; (2), 14·742 grms. bichromate of potassium, made up to 1 litre with water; 1 c.c. of this = 0·0085 grm. $NaNO_3$, or 0·0101 grm. KNO_3. This strength, as recommended by Dr. Attfield, is very convenient.

If a nitrated manure is being examined, 10 grms. may be taken, treated with water, and filtered into a 200 c.c. flask, washed, and made up to the mark. The analysis is carried out thus:—50 c.c. of the iron solution with 20 c.c. (= 1 grm. manure) are run into the flask, the stopper inserted, and the flask placed on a sand-bath, the contents boiled till the liquid is so thick that semi-solid drops are splashed against the sides; the flask is then removed, a cloth put round it as there is danger of explosion, allowed to cool for some time; 100 c.c. of water then run in, and the titration with bichromate of potash solution carried out.

The following example will give an idea of the accuracy of this method under these conditions:—20 c.c. (= 1 grm. manure) treated as above, with 50 c.c. iron solution, 31 c.c. of bichromate required to oxidise the excess of ferrous iron. A blank titration showed that 50 c.c. iron = 54 c.c. bichromate; therefore 54 − 31 = 23 c.c. bichromate to complete oxidation, 23 × 0·0085 = 0·1955, or 19·55 per cent $NaNO_3$ in the manure. As the sample operated on was mixed carefully, thus—

20	parts 95·5 per cent	$NaNO_3$
80	,,	ammoniacal guano
100		

the calculated amount is 19·10 per cent $NaNO_3$, so the result, considering the well-known difficulty of this process is not unsatisfactory; the error, being less than 0·1 per cent of the nitrogen, if recorded as ammonia. In standardising the iron solution, I boil, say, 50 c.c., and on cooling titrate with bichromate, thus having about the same conditions in the trial and actual determination. The semi-solid matter in the flask is not very readily soluble; but this does not appear very necessary, as I am inclined to think the ferrous iron is immediately dissolved, which is all that is required. It is well to fix the end-point when a bright yellow colour is shown with a drop of ferricyanide on the slab.

Lawes' Works, Barking, Essex,
June 14, 1895.

POTASSIUM TETRAOXALATE AS A STANDARD IN ACIDIMETRY.

By ARTHUR BORNTRAEGER.

H. BORNTRAEGER (*Chemiker Zeitung*, 1881, 519), as far as I know, was the first to propose the acid tartrate of potassium as a standard for alkali solutions. In 1892, I explained (*Zeit. f. Anal. Chemie*, 1892, 43) why I preferred it for that purpose to other substances, and also to the tetraoxalate of potassium. I gave then, and on other occasions (*Zeit. f. Anal. Chemie*, 1886, 327; *Zeit. f. Angewandte Chemie*, 1894, 54), special weight to the following facts:—

That the acid tartrate, which crystallises free from water, is easily obtained in a pure state; that it is scarcely hygroscopic; and that the dry salt may be preserved without alteration.

In mentioning the tetraoxalate amongst the substances that have been proposed by others, I objected (*Zeit. f. Anal. Chemie*, 1892, 43) that it contains water, and therefore might be liable to effloresce. It would be necessary, therefore, as I observed, either to make use of the dried salt or to determine each time the proportion of water. It is generally admitted that this salt loses its water when heated to 128° C. It further resulted from my paper that I did not consider it an easy thing to purify the tetraoxalate.

Wells (*Journ. Anal. and Appl. Chem.*, vi., 1892, 191) recognises the difficulties in preparing pure potassium tetraoxalate, and points out the tendency of this salt to effloresce. It was only through abstracts in a chemical journal (*Zeit. f. Anal. Chemie*, 1893, 452; 1894, 456) that I first became acquainted with the paper by Wells and a paper by B. C. Hinman (*Journ. Anal. and Appl. Chem.*, vi., 1892, 435). Of the latter I heard only recently. I have, however, read lately the original papers of both authors. Hinman, confirming, by his researches, those of W. Frear (*Vide* U.S. Department of Agriculture, Division of Chemistry, *Bulletin* No. 31, "Proceedings of the Eighth Annual Convention of the Association of Official Agricultural Chemists," August 13, 14, and 15, 1891, p. 131), concludes that potassium tetraoxalate is not adaptable as a standard for alkali solutions, since the preparation of that salt in a pure state offers great difficulties. He further points out that the salt in the dried state is hygroscopic, and that the salt containing water tends to effloresce.

As to Hinman's researches about the desiccation of the tetraoxalate at 128° C., I observe that I had not myself undertaken any experiments upon that question. That the salt gives off its water of crystallisation at that temperature is a fact I had simply taken from the best authorities (Gmelin, "Handbuch der Chemie," iv., 1848, 831; Wurtz, "Dictionnaire de Chimie, Pure et Appliquée," ii., 680; Watts, "Dictionary of Chemistry," 2nd ed., iv., 1883, 264). Gmelin (*loc. cit.*) attributes that assertion to Berzelius. I cannot, therefore, take upon myself any responsibility on that point, in which I simply relied on the exactitude of those who had studied the question.

Gabinetto di Tecnologia della R. Scuola
Superiore di Agricultura in Portici.

A REFORM IN CHEMICAL, PHYSICAL, AND TECHNICAL CALCULATIONS.

By C. J. HANSSEN, C.E.

(Continued from p. 164).

By similar calculation as used at p. 164 we find at normal atmospheric density and 0° N = 273° N absolute temperature, the weight and volume of compound gases. (See Table).

Heat.

If the specific heat of water at freezing-point is = 1, then the specific heat of hydrogen at constant pressure is = 3·400. For hydrogen, oxygen, carbon, nitrogen, and other simple gases, and for compounds which, in combining, have retained the original volume of the components, such as CO, is γ, or the ratio between specific heat at constant pressure and at constant volume exactly

$$17 : 12 = 1{\cdot}4166666 : 1.$$

The caloric work required to heat 1 kilogrm. H 1° N. consequently is:—

At constant pressure (heating and expanding) .. .. .. = 3·400 cal. = 17/5 calor.
At constant volume (heating without expanding) 3·400 cal. × 12/17 .. .. = 2·400 „ = 12/5 „
The difference (expanding without heating) is 3·400 cal. × 5/17 .. .. = 1·000 „ = 5/5 „

1 kilogrm. hydrogen is = 56/5 cbm.; consequently, to heat 1 cbm. H, of normal atmospheric density and 0° N., 1° N. requires—

At constant pressure.. .. $\frac{17\times5}{5\times56} = 17/56$ calor.
At constant volume .. .. $\frac{12\times5}{5\times56} = 12/56$ „
Expanding the volume .. $\frac{5\times5}{5\times56} = 5/56$ „

For other simple gases and for compounds which have retained their original volume, we find the heat required per kilogrm. by dividing the figures found per kilogrm. hydrogen by the relative weight of the gas in question.

Thus, per kilogrm. oxygen, is required—

At constant pressure.. .. $\frac{17}{5\times16} = 17/80$ calor.
At constant volume .. .. $\frac{12}{5\times16} = 12/80$ „
For expansion only .. .. $\frac{5}{5\times16} = 5/80 = \frac{1}{16}$ „

To heat 1 cbm. of these gases (of normal density and temperature) 1° N. is required—exactly the same quantity of heat as for 1 cbm. of hydrogen.

Heating of *compound gases* which in combining have contracted in volume, requires per kilogrm.:—

At constant pressure $\frac{17}{5}$ cal. $\times \frac{\text{ratio of contraction}}{\text{relative weight}} = x$ cal.
At constant volume $\frac{12}{5}$ cal. $\times \frac{\text{ratio of contraction}}{\text{relative weight}} = x$ „
For expansion only $\frac{5}{5}$ cal. $\times \frac{\text{ratio of contraction}}{\text{relative weight}} = x$ „

and per cbm. of normal density and temperature is required the same quantity of heat as for hydrogen *multiplied* by the ratio of contraction of the gas in question.

Compound gases.		Ratio of contraction.	Relative weight.	1 cbm. weighs kilog. 1 litre = grm.	1 kilog. contains cbm. 1 grm. „ litre.
Carbon monoxide,	CO	1 : 1	14	70/56 = 5/4	56/70 = 4/5 = 0·80000
Carbon dioxide,	CO_2	1½ : 1	22	110/56	56/110 = 0·50909
Methane,	CH_4	2½ : 1	8	40/56 = 5/7	56/40 = 7/5 = 1·40000
Acetylene,	C_2H_2	2 : 1	13	65/56	56/65 = 0·86154
Ethylene,	C_2H_4	3 : 1	14	70/56 = 5/4	56/70 = 4/5 = 0·80000
Ethane,	C_2H_6	4 : 1	15	75/56	56/75 = 0·74666
Allylene,	C_3H_4	3½ : 1	20	100/56 = 25/14	56/100 = 14/25 = 0·56000
Propylene,	C_3H_6	4½ : 1	21	105/56 = 15/8	56/105 = 8/15 = 0·53333
Propane,	C_3H_8	5½ : 1	22	110/56	56/110 = 28/55 = 0·50909
Elayl,	C_4H_8	3 : 1	14	70/56 = 5/4	56/70 = 4/5 = 0·80000
Butylene,	C_4H_8	6 : 1	28	140/56 = 5/2	56/140 = 2/5 = 0·40000
Butane,	C_4H_{10}	7 : 1	29	145/56	56/145 = 0·31500
Pentane,	C_5H_{12}	8½ : 1	36	180/56 = 45/14	56/180 = 14/45 = 0·31111
Benzene,	C_6H_6	6 : 1	39	195/56	56/195 = 0·28718
Dipropyl,	C_6H_{14}	10 : 1	43	215/56	56/215 = 0·26046
Sulphide of Hydr.,	SH_2	1½ : 1	17	85/56	56/85 = 0·65882
Ammonia,	NH_3	2 : 1	17/2	85/112	112/85 = 1·31765
Vapour of water,	H_2O	1½ : 1	9	45/56	56/45 = 1·24444

Thus, for *acetylene*—

	Per 1 kilogrm.	Per 1 cbm.
At constant pressure	$\frac{17}{5}\times\frac{2}{13}=34/65$ cal.	$\frac{17}{56}\times 2=17/28$cal.
At constant volume	$\frac{12}{5}\times\frac{2}{13}=24/65$ „	$\frac{12}{56}\times 2=12/28$ „
For expanding only	$\frac{5}{5}\times\frac{2}{13}=10/65$ „	$\frac{5}{56}\times 2=5/28$ „

For *vapour of water*, H_2O,—

	Cal.	Cal.
At constant pressure ..	$\frac{17}{5}\times\frac{1\frac{1}{2}}{9}=17/30$	$\frac{17}{56}\times 1\frac{1}{2}=51/112$
At constant volume ..	$\frac{12}{5}\times\frac{1\frac{1}{2}}{9}=12/30=\frac{2}{5}=0{\cdot}4$	$\frac{12}{56}\times 1\frac{1}{2}=36/112$
For expanding only	$\frac{5}{5}\times\frac{1\frac{1}{2}}{9}=5/30=\frac{1}{6}$	$\frac{5}{56}\times 1\frac{1}{2}=15/112$

Ice and *liquid water* hermetically inclosed are H_2O at constant volume.

Errata.—In the Table at foot of page 163, 3rd line, "10·7" should read "10/7"; 4th line, "4/5" should read "5/4."

(To be continued).

3, Valdemarsgade, Copenhagen, V.
May 6, 1895.

LONDON WATER SUPPLY.

Report on the Composition and Quality of Daily Samples of the Water Supplied to London for the Month Ending May 31st, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To Major-General A. De Courcy Scott, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 14th, 1895.

Sir,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The whole of the 189 samples examined were found to be clear, bright, and efficiently filtered.

The month of May has been remarkably dry, the total rainfall at Oxford, representing the Thames valley, being only 0·16 inch. As the 25 years' mean for the month is 1·95 inch, the deficiency is no less than 1·79 inch. What little rain there was fell on four days, the 1st, 17th, 23rd, and 30th.

It has usually been found that the river water in dry summer months is of a somewhat higher degree of purity than when the summer is wet. On comparing the chemical composition of the waters during May with their composition in April when the mean amount of rain fell, it will be seen that the improvement, although perceptible, is not so striking as it formerly was when the present high degree of purity was not so uniformly reached. It therefore appears that the filtering plant of the several Companies is quite sufficient to preserve the high standard of purity, irrespective of occasional influxes into the river of vegetable and peaty organic matter due to sudden or long-continued rain. The chief improvement is in the organic carbon and the colour.

On the other hand, bacteriological examinations show the improvement due to the dry season in a marked manner. The filtered water from the general wells at the works during the month of May contained an average of 18 microbes per cubic centimetre, as against 46 in the month of April, whilst the unfiltered water contained 4070 per cubic centimetre.

We are, Sir,
Your obedient Servants,
William Crookes.
James Dewar.

THE OXYHYDROGEN ACCUMULATOR.

By H. N. WARREN, Research Analyst.

Grove's oxyhydrogen battery, better known as the gas battery, in its simplest form consists of two strips of platinum foil, each strip being exposed, one to the action of hydrogen gas, the other to that of oxygen, contained in suitable receptacles.

Based upon a somewhat similar theory, while at the same time taking advantage of the peculiar surface action that the element palladium exerts when exposed to an atmosphere of hydrogen, the author has constructed batteries according to the following method:—He takes an ordinary Woulff's bottle containing acidulated water, into which are inserted two tubes, constructed by fusing into the glass tubes two platinum wires, terminating in a platinum plate for the oxygen tube, and one of palladium for the hydrogen tube, each tube being filled with its respective gas. Several cells thus arranged in series have been found to produce a mean voltage of 0·45, while by rendering the surface more active even 0·5 has been attained, a series of five such batteries being capable of decomposing water. The next experiments performed were with a view of increasing the pressure of each gas, and here the first danger presents itself,

Subjected to 180 atmospheres pressure, the mixed gases had been found on previous occasions to unite with great violence, whereas by increased surface action they combine at even diminished pressure. At the same time, the consumption of hydrogen being double that of the oxygen in its union to form water, a further difficulty presents itself as regards regulating the pressure; and in order to produce a greater surface action plates of graphite were prepared, some platinised and others palladinised, each being exposed to the action of its respective gas by enclosing the same in steel canisters lined with lead, and furnished with a water-gauge in order to indicate the level and ensure the existence of an even pressure.

Both gases were now introduced under two atmospheres pressure, and were somewhat quickly absorbed, an increase of every two atmospheres increasing the voltage by about 0·15 volt, until 1 volt was reached, and in one case even 1·25 was attained.

Experiments are now being carried out with respect to maintaining a more steady pressure, and to rendering the apparatus less dangerous as regards an explosive mixture being formed; when this is accomplished, together with the removal of other small difficulties which still exist, it will probably be possible to construct a self-charging accumulator.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

ARGON.*

By the Right Hon. LORD RAYLEIGH, M.A., D.C.L., LL.D., F.R.S., Professor of Natural Philosophy, R.I.

(Concluded from p. 302).

I have said enough about this method, and I must now pass on to the alternative method which has been very successful in Professor Ramsay's hands—that of absorbing nitrogen by means of red-hot magnesium. By the kindness of Professor Ramsay and Mr. Matthews, his assistant, we have here the full scale apparatus before us almost exactly as they use it. On the left there is a reservoir of nitrogen derived from air by the simple removal of oxygen. The gas is then dried. Here it is bubbled through sulphuric acid. It then passes through a long tube made of hard glass and charged with magnesium in the form of thin turnings. During the passage of the gas over the magnesium at a bright red heat, the nitrogen is absorbed in a great degree, and the gas which finally passes through is immensely richer in argon than that which first enters the hot tube. At the present time you see a tolerably rapid bubbling on the left, indicative of the flow of atmospheric nitrogen into the combustion furnace; whereas, on the right, the outflow is very much slower. Care must be taken to prevent the heat rising to such a point as to soften the glass. The concentrated argon is collected in a second gasholder, and afterwards submitted to further treatment. The apparatus employed by Professor Ramsay in the subsequent treatment is exhibited in the diagram, and is very effective for its purpose; but I am afraid that the details of it would not readily be followed from any explanation that I could give in the time at my disposal. The principle consists in the circulation of the mixture of nitrogen and argon over hot magnesium, the gas being made to pass round and round until the nitrogen is effectively removed from it. At the end that operation, as in the case of the oxygen method, proceeds somewhat slowly. When the greater part of the nitrogen is gone, the remainder seems to be unwilling to follow, and it requires somewhat protracted treatment in order to be sure that the nitrogen has wholly disappeared. When I say "wholly disappeared," that perhaps would be too much to say in any case. What we can say is, that the spectrum test is adequate to show the presence, or at any rate to show the addition, of about one-and-a-half per cent of nitrogen to argon as pure as we can get it; so that it is fair to argue that any nitrogen at that stage remaining in the argon is only a small fraction of one-and-a-half per cent.

I should have liked at this point to be able to give advice as to which of the two methods—the oxygen method or the magnesium method—is the easier and the more to be recommended; but I confess that I am quite at a loss to do so. One difficulty in the comparison arises from the fact that they have been in different hands. As far as I can estimate, the quantities of nitrogen eaten up in a given time are not very different. In that respect, perhaps, the magnesium method has some advantage; but, on the other hand, it may be said that the magnesium process requires a much closer supervision, so that, perhaps, fourteen hours of the oxygen method may not unfairly compare with eight hours or so of the magnesium method. In practice a great deal would depend upon whether in any particular laboratory alternate currents are available from a public supply. If the alternate currents are at hand, I think it may probably be the case that the oxygen method is the easier; but, otherwise, the magnesium method would probably be preferred, especially by chemists who are familiar with operations conducted in red-hot tubes.

I have here another experiment illustrative of the reaction between magnesium and nitrogen. Two rods of that metal are suitably mounted in an atmosphere of nitrogen, so arranged that we can bring them into contact and cause an electric arc to form between them. Under the action of the heat of the electric arc the nitrogen will combine with the magnesium; and if we had time to carry out the experiment we could demonstrate a rapid absorption of nitrogen by this method. When the experiment was first tried, I had hoped that it might be possible, by the aid of electricity, to start the action so effectively that the magnesium would continue to burn independently under its own developed heat in the atmosphere of nitrogen. Possibly, on a larger scale, something of this sort might succeed, but I bring it forward here only as an illustration. We turn on the electric current, and bring the magnesiums together. You see a brilliant green light, indicating the vaporisation of the magnesium. Under the influence of the heat the magnesium burns, and there is collected in the glass vessel a certain amount of brownish-looking powder which consists mainly of the nitride of magnesium. Of course, if there is any oxygen present it has the preference, and the ordinary white oxide of magnesium is formed.

The gas thus isolated is proved to be inert by the very fact of its isolation. It refuses to combine under circumstances in which nitrogen, itself always considered very inert, does combine, both in the case of the oxygen treatment and in the case of the magnesium treatment; and these facts are, perhaps, almost enough to justify the name which we have suggested for it. But, in addition to this, it has been proved to be inert under a considerable variety of other conditions such as might have been expected to tempt it into combination. I will not recapitulate all the experiments which have been tried, almost entirely by Professor Ramsay, to induce the gas to combine. Hitherto, in our hands, it has not done so; and I may mention that recently, since the publication of the abstract of our paper read before the Royal Society, argon has been submitted to the action of titanium at a red heat, titanium being a metal having a great affinity for nitrogen, and that argon has resisted the temptation to which nitrogen succumbs. We never have asserted, and we do not now assert, that argon can under no circumstances be got to combine. That would, indeed, be a rash assertion for any one to venture upon; and only within the last few weeks there has been a most interesting announcement by M. Berthelot, of Paris, that, under the action of the silent electric discharge, argon can be absorbed when treated in contact with the vapour of benzine. Such a statement, coming from so great an authority, commands our attention; and if we accept the conclusion, as I suppose we must do, it will follow that argon has, under those circumstaces, combined.

Argon is rather freely soluble in water. That is a thing that troubled us at first in trying to isolate the gas; because, when one was dealing with very small quantities, it seemed to be always disappearing. In trying to accumulate it we made no progress. After a sufficient quantity had been prepared, special experiments were made on the solubility of argon in water. It has been found that argon, prepared both by the magnesium method and by the oxygen method, has about the same solubility in water as oxygen—some two-and-a-half times the solubility of nitrogen. This suggests, what has been verified by experiment, that the dissolved gases of water should contain a larger proportion of argon than does atmospheric nitrogen. I have here an apparatus of a somewhat rough description, which I have employed in experiments of this kind. The boiler employed consists of an old oil-can. The water is supplied to it and drawn from it by coaxial tubes of metal. The incoming cold water flows through the outer annulus between the two tubes. The outgoing hot water passes through the inner tube, which ends in the interior of the vessel at a higher level. By means of this arrangement the heat of the water which has done its work is passed on to the incoming water not yet in operation, and in that way a limited amount of heat is made

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* A Lecture delivered at the Royal Institution of Great Britain Friday, April 5, 1895.

to bring up to the boil a very much larger quantity of water than would otherwise be possible, the greater part of the dissolved gases being liberated at the same time. These are collected in the ordinary way. What you see in this flask is dissolved air collected out of water in the course of the last three or four hours. Such gas, when treated as if it were atmospheric nitrogen, that is to say after the removal of the oxygen and minor impurities, is found to be decidedly heavier than atmospheric nitrogen to such an extent as to indicate that the proportion of argon contained is about double. It is obvious, therefore, that the dissolved gases of water form a convenient source of argon, by which some of the labour of separation from air is obviated. During the last few weeks I have been supplied from Manchester by Mr. Macdougall, who has interested himself in this matter, with a quantity of dissolved gases obtained from the condensing water of his steam-engine.

As to the spectrum, we have been indebted from the first to Mr. Crookes, and he has been good enough to-night to bring some tubes which he will operate, and which will show you at all events the light of the electric discharge in argon. I cannot show you the spectrum of argon, for unfortunately the amount of light from a vacuum tube is not sufficient for the projection of its spectrum. Under some circumstances the light is red, and under other circumstances it is blue. Of course when these lights are examined with the spectroscope—and they have been examined by Mr. Crookes with great care—the differences in the colour of the light translate themselves into different groups of spectrum lines. We have before us Mr. Crookes's map, showing the two spectra upon a very large scale. The upper is the spectrum of the blue light; the lower is the spectrum of the red light; and it will be seen that they differ very greatly. Some lines are common to both; but a great many lines are seen only in the red, and others are seen only in the blue. It is astonishing to notice what trifling changes in the conditions of the discharge bring about such extensive alterations in the spectrum.

One question of great importance, upon which the spectrum throws light is, Is the argon derived by the oxygen method really the same as the argon derived by the magnesium method? By Mr. Crookes's kindness I have had an opportunity of examining the spectra of the two gases side by side, and such examination as I could make revealed no difference whatever in the two spectra, from which, I suppose, we may conclude either that the gases are absolutely the same, or, if they are not the same, that at any rate the ingredients by which they differ cannot be present in more than a small proportion in either of them.

My own observations upon the spectrum have been made principally at atmospheric pressure. In the ordinary process of sparking, the pressure is atmospheric; and, if we wish to look at the spectrum, we have nothing more to do than to include a jar in the circuit, and to put a direct-vision prism to the eye. At my request, Professor Schuster examined some tubes containing argon at atmospheric pressure prepared by the oxygen method, and I have here a diagram of a characteristic group. He also placed upon the sketch some of the lines of zinc, which were very convenient, as directing one exactly where to look. (See Fig.).

Within the last few days, Mr. Crookes has charged a radiometer with argon. When held in the light from the electric lamp, the vanes revolve rapidly. Argon is anomalous in many respects, but not, you see, in this.

Next, as to the density of argon. Professor Ramsay has made numerous and careful observations upon the density of the gas prepared by the magnesium method, and he finds a density of about 19·9 as compared with hydrogen. Equally satisfactory observations upon the gas derived by the oxygen method have not yet been made, but there is no reason to suppose that the density is different, such numbers as 19·7 having been obtained.

One of the most interesting matters in connection with argon, however, is what is known as the ratio of the specific heats. I must not stay to elaborate the questions involved, but it will be known to many who hear me that the velocity of sound in a gas depends upon the ratio of two specific heats—the specific heat of the gas measured at constant pressure, and the specific heat measured at constant volume. If we know the density of a gas, and also the velocity of sound in it, we are in a position to infer this ratio of specific heats; and by means of this method, Professor Ramsay has determined the ratio in the case of argon, arriving at the very remarkable result that the ratio of specific heats is represented by the number 1·65, approaching very closely to the theoretical limit, 1·67. The number 1·67 would indicate that the gas has no energy except energy of translation of its molecules. If there is any other energy than that, it would show itself by this number dropping below 1·67. Ordinary gases, oxygen, nitrogen, hydrogen, &c., do drop below, giving the number 1·4. Other gases drop lower still. If the ratio of specific heats is 1·65, practically 1·67, we may infer then that the whole energy of motion is translational; and from that it would seem to follow by arguments which, however, I must not stop to elaborate, that the gas must be of the kind called by chemists monatomic.

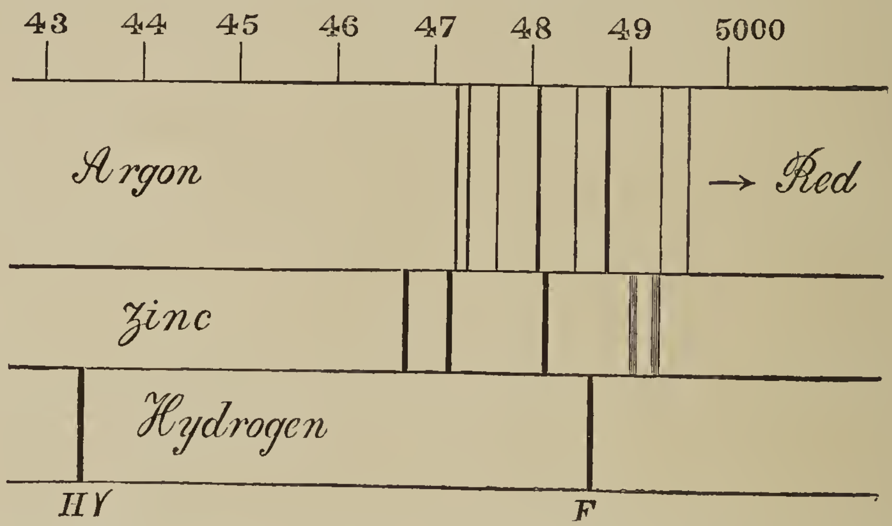
I had intended to say something of the operation of determining the ratio of the specific heats, but time will not allow. The result is, no doubt, very awkward. Indeed, I have seen some indications that the anomalous properties of argon are brought as a kind of accusation against us. But we had the very best intentions in the matter. The facts were too much for us; and all we can do now is to apologise for ourselves and for the gas.

Several qnestions may be asked, upon which I should like to say a word or two, if you will allow me to detain you a little longer. The first question (I do not know whether I need ask it) is, Have we got hold of a new gas at all? I had thought that that might be passed over, but only this morning I read in a technical journal the suggestion that argon was our old friend nitrous oxide. Nitrous oxide has roughly the density of argon; but that, as far as I can see, is the only point of resemblance between them.

Well, supposing that there is a new gas, which I will not stop to discuss, because I think the spectrum alone would be enough to prove it, the next question that may be asked is, Is it in the atmosphere? This matter naturally engaged our earnest attention at an early stage of the enquiry. I will only indicate in a few words the arguments which seem to us to show that the answer must be in the affirmative.

In the first place, if argon be not in the atmosphere, the original discrepancy of densities which formed the starting point of the investigation remains unexplained, and the discovery of the new gas has been made upon a false clue. Passing over that, we have the evidence of the blank experiments, in which nitrogen originally derived from chemical sources is treated either with oxygen or with magnesium, exactly as atmospheric nitrogen is treated. If we use atmospheric nitrogen, we get a certain proportion of argon, about 1 per cent. If we treat chemical nitrogen in the same way we get, I will not say absolutely nothing, but a mere fraction of what we should get had atmospheric nitrogen been the subject. You may ask, Why do we get any fraction at all from chemical nitrogen? It is not difficult to explain the small residue, because in the manipulation of the gases large quantities of water are used; and, as I have already explained, water dissolves argon somewhat freely. In the processes of manipulation some of the argon will come out of solution, and it remains after all the nitrogen has been consumed.

Another wholly distinct argument is founded upon the method of diffusion introduced by Graham. Graham showed that if you pass gas along porous tubes you alter the composition, if the gas is a mixture. The lighter constituents go more readily through the pores than do the heavier ones. The experiment takes this form:—A number of tobacco-pipes—eight in the actual arrangement—are joined together in series with indiarubber junctions, and they are put in a space in which a vacuum can be made, so that the space outside the porous space is vacuous or approximately so. Through the pipes ordinary air is led. One end may be regarded as open to the atmosphere. The other end is connected with an aspirator so arranged that the gas collected is only some two per cent of that which leaks through the porosities. The case is like that of an Australian river drying up almost to nothing in the course of its flow. Well, if we treat air in that way, collecting only the small residue which is less willing than the remainder to penetrate the porous walls, and then prepare "nitrogen" from it by removal of oxygen and moisture, we obtain a gas heavier than atmospheric nitrogen, a result which proves that the ordinary nitrogen of the atmosphere is not a simple body, but is capable of being divided into parts by so simple an agent as the tobacco-pipe.



If it be admitted that the gas is in the atmosphere, the further question arises as to its nature.

At this point I would wish to say a word of explanation. Neither in our original announcement at Oxford, nor at any time since, until the 31st of January, did we utter a word suggesting that argon was an element; and it was only after the experiments upon the specific heats that we thought that we had sufficient to go upon in order to make any such suggestion in public. I will not insist that that observation is absolutely conclusive. It is certainly strong evidence. But the subject is difficult, and one that has given rise to some difference of opinion among physicists. At any rate this property distinguishes argon very sharply from all the ordinary gases.

One question which occurred to us at the earlier stage of the enquiry, as soon as we knew that the density was not very different from 21, was the question of whether, possibly, argon could be a more condensed form of nitrogen, denoted chemically by the symbol N_3. There seem to be several difficulties in the way of this supposition. Would such a constitution be consistent with the ratio of specific heats (1·65)? That seems extremely doubtful. Another question is, Can the density be really as high as 21, the number required on the supposition of N_3? As to this matter, Professor Ramsay has repeated his measurements of density, and he finds that he cannot get even so high as 20. To suppose that the density of argon is really 21, and that it appears to be 20 in consequence of nitrogen still mixed with it, would be to suppose a contamination with nitrogen out of all proportion to what is probable. It would mean some 14 per cent of nitrogen, whereas it seems that from one-and-a-half to two per cent is easily enough detected by the spectroscope. Another question that may be asked is, Would N_3 require so much cooling to condense it as argon requires?

There is one other matter on which I would like to say a word—the question as to what N_3 would be like if we had it. There seems to be a great discrepancy of opinions. Some high authorities, among whom must be included, I see, the celebrated Mendeleeff, consider that N_3 would be an exceptionally stable body; but most of the chemists with whom I have consulted are of opinion that N_3 would be explosive, or, at any rate, absolutely unstable. That is a question which may be left for the future to decide. We must not attempt to put these matters too positively. The balance of evidence still seems to be against the supposition that argon is N_3, but for my part I do not wish to dogmatise.

A few weeks ago we had an eloquent lecture from Prof. Rücker on the life and work of the illustrious Helmholtz. It will be known to many that during the last few months of his life Helmholtz lay prostrate in a semi-paralysed condition, forgetful of many things, but still retaining a keen interest in science. Some little while after his death we had a letter from his widow, in which she described how interested he had been in our preliminary announcement at Oxford upon this subject, and how he desired the account of it to be read to him over again. He added the remark, "I always thought that there must be something more in the atmosphere."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 6th, 1895.

Mr. A. G. Vernon Harcourt, President, in the Chair.

Messrs. G. E. Shaw, H. Thornton, and H. F. A. Wigley were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. George Percy Bailey, B.A., 7, Mount Pleasant Square, Dublin; Charles James Fawel, The Laboratory, Cranford, Middlesex; Jervis E. Foakes, Medical School, Caxton Street, Westminster, S.W.; Stanley Fox, 46, Preston Street, Faversham: Rev. Henry Arthur Hall, M.A., The Schoolhouse, Totnes; James Henderson, B.Sc., 193, Blackness Road, Dundee; William Henry Pennington, Firedhouse, Rochdale; W. T. B. Ridge, 2, Ashwood Terrace, Longton, Staffs.; William Augustus Rugginz, 114, Upton Lane, Forest Gate, E.; W. T. Tibbald, 72, Lafayette Avenue, Detroit, U.S.A.; Harold E. Wright, Springhurst, Hartburn, Stockton-on-Tees.

It was announced from the Chair that on Thursday, June 20th, an Extraordinary General Meeting of the Society would be held at 8 p.m., to vote on the following change in the Bye-law which is proposed by the Council:—

In Bye-law 1 to strike out the last paragraph, beginning "The life composition fee," and insert the following:—"The life composition fee shall be £30, excepting that Fellows who have paid ten annual subscriptions shall pay as life composition fee £20; Fellows who have paid fifteen annual subscriptions shall pay £15; Fellows who have paid twenty annual subscriptions shall pay £12; and Fellows who have paid twenty-five annual subscriptions shall pay £10."

Of the following papers those marked * were read:—

*74. *The Molecular Refractions of Dissolved Salts and Acids.*" By Dr. J. H. Gladstone, F.R.S., and Walter Hibbert.

In a paper on the "Refraction Equivalents of the Elements" (*Phil. Trans.*, 1870), Dr. Gladstone gave reasons for believing that the molecular refraction of a salt or acid is not altered when dissolved in water. Some controversy arose upon this point, and the refraction of salts in solution has been the subject of investigation by many experimenters. The present communication is devoted to a rigid examination of two of the reasons previously assigned:—

1st. The similarity of the molecular refraction of substances when determined from the solid and from its solution.

2nd. That the molecular refraction of a dissolved salt is not affected by varying the amount of water.

The data employed in the present investigation are:—Dr. Gladstone's former observations of 1869 and 1891, wherever sufficiently reliable; the published observations of other experimenters; and numerous series of observations recently made by Mr. Hibbert.

The results are arranged in tables. One of these exhibits the refraction values of all the solid salts which have been determined, provided they have but one index of refraction, together with a few others. These are compared with the refraction of the same salt in a nearly saturated solution. Another gives the same for anhydrous acids and their strong solutions. A third shows the effect upon refraction of diluting a strong solution of the salt or acid.

The combined results of these investigations are made apparent to the eye in five diagrams containing respectively the principal observations on the chlorides, the other haloid salts, the nitrates, the sulphates, and the acids themselves. These diagrams represent the specific refractive energy of the substance before solution, and then upon the addition of varying proportions of water. By far the greatest change occurs with hydrochloric acid, which rises from 0·30 to nearly 0·39 when dissolved in 1·5 times its weight of water, and to 0·40 in very dilute solutions. Many other salts and acids show a distinct, but much smaller, increase, while in others, again, if there be any change, it is within the limits of errors of observation. Various points of relationship between these variations and the chemical nature of the binary compounds examined are pointed out.

This investigation explains some of the difficulties met with in the original determinations of refraction equivalents, and will be of great service in any future revision of them.

The general conclusion is that when a salt or acid dissolves in water the law of permanency of specific refractive energy, notwithstanding change of physical condition, does hold good; but that in many, if not most, cases there is some circumstance which causes a slight departure from it, while with the "strong acids" the departure is considerable. This change takes place principally in the initial stage of solution of the solid or liquid compound; but in many cases a small further change is discernible as more and more water is added; but this soon becomes inappreciable. This change is, in some cases, in the direction of an increased refraction, especially in the haloid salts and the acids; in other cases, especially the nitrates and salts of low refractive energy, this change is in the opposite direction. In either case the dilution effect is in the same direction as that due to solution. In a few cases, where the dispersion was capable of being estimated, the change in it was found to be proportionally greater than the change in the refraction itself. The origin of this refraction change is at present obscure, but it probably arises from some gradual change in the arrangement of the atoms or molecules of the salt or acid under the influence of water; and there are clear indications of some connection between the amount of this change and the amount of the specific refractive energy of the salts themselves. It stands also in some relation to the phenomena of electric conductivity, and especially of magnetic rotation.

*75. "*A Comparison of some Properties of Acetic Acid, and its Chloro- and Bromo-derivatives.* By S. U. Pickering, F.R.S.

The properties which have been examined are, in the cases of acetic acid and its chloro-derivatives, the heat of fusion, heat capacities both as solids and liquids, heat of dissolution, heat of dilution, and freezing-points when mixed with water; the boiling-points, densities, and magnetic rotations are also compared with these. In the case of the bromo-derivatives, the heat of dissolution of the solids alone was determined.

As regards the boiling-point, heat capacity of liquid, density, and heat of dissolution, acetic acid appears to occupy an exceptional position when compared with its chloro-derivatives, whereas, as regards the freezing-point, magnetic rotation, and heat of dilution, the alternate members of the series show a close relationship with each other.

Monochloracetic acid was found to exist in four distinct crystalline modifications, differing from each other in their melting-points by about 5°. Any of these modifications can be obtained at will, either from the liquid acid or from mixtures of it with water. The most stable form (the α) possesses a heat of fusion, and, hence, a heat of dissolution, when solid, about 500 cal. greater (negatively) than that of the β-modification; and from the fact that the heat absorbed on dissolution appears to be exceptionally large when compared with that absorbed by the other chlorinated acids, it is probable that these are in a form comparable with one of the less stable modifications of chloracetic acid. A similar exceptional position is occupied by monobromacetic acid amongst its congeners, but all attempts to obtain other modifications of this acid failed.

76. "*$\beta\beta$-Dinaphthyl and its Quinones.*" By F. D Chattaway, B.A.

Although several substances of the compositon $C_{20}H_{14}$, differing considerably in melting-point and physical properties, have been prepared, the constitution of only one of these, $\alpha\alpha$-dinaphthyl, is known.

The present paper contains an account of the synthesis of $\beta\beta$-dinaphthyl, of its qninones, and of some closely-related derivatives.

$\beta\beta$-Dinaphthyl is obtained by the action of sodium on β-chloronapththalene dissolved in boiling xylene in presence of a small quantity of ethyl acetate. It is also produced when zinc-dust acts on β-diazonaphthalene sulphate dissolved in alcohol. It crystallises well and completely from benzene or xylene, in large, colourless plates, having a slight blue fluorescence. It is easily soluble in boiling benzene, xylene, and glacial acetic acid, much less soluble in alcohol. It sublimes readily, but is not volatile with steam. It melts at 183·5°, and boils at 452° under a pressure of 753 m.m. Its molecular weight, determined by the depression of the freezing-point of a benzene solution, agrees very closely with the calculated number.

When dissolved in glacial acetic acid and oxidised by chromic acid, one or other of two quinones can be obtained, according to the conditions under which the oxidation is performed. If the oxidation be effected rapidly in boiling glacial acetic acid, a quinone is produced in almost theoretical quantities, whose composition and molecular weight agree with the formula $C_{20}H_{12}O_2$. This is an orange-yellow substance, melting at 177°, and crystallising in very small needles, generally aggregated into rosettes. It is easily soluble in alcohol, ethyl acetate, glacial acetic acid, and benzene. It yields a colourless hydroquinone on reduction, and dissolves easily in cold concentrated sulphuric acid with a very characteristic indigo-blue colour. Its appearance and behaviour lead to the conclusion that it is a paraquinone analogous to α-naphthoquinone (1 . 4) having the constitution—

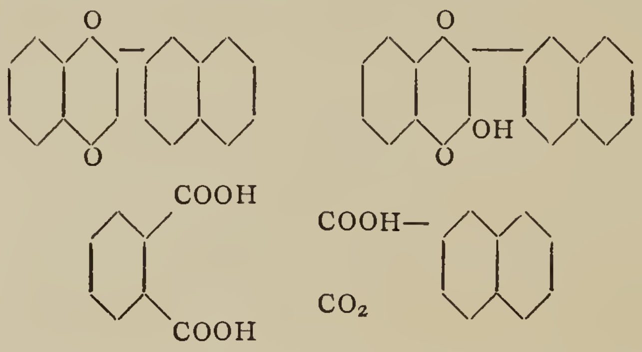
$$C_{10}H_5O{\cdot}C_{10}H_7{\cdot}O \ (1 . 2 . 4).$$

When this quinone is heated with a solution of potassium hydroxide, one of its hydrogen atoms is displaced, the hydrogen liberated reducing the quinone—

$$C_{20}H_{12}O_2 + KOH = C_{20}H_{11}(OH)_2OK.$$

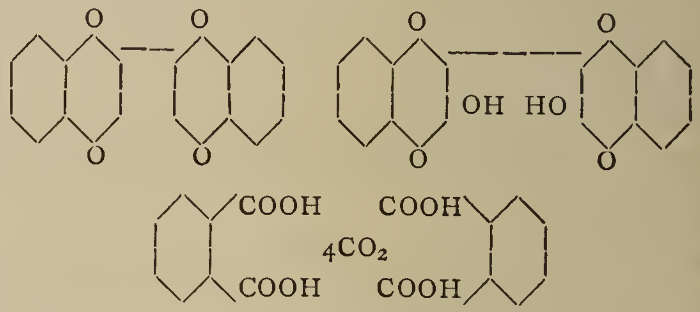
If this action takes place in presence of air, the two hydroxyl groups are at once oxidised, the potassium derivative, $C_{20}H_{11}O_2(OK)$, of a hydroxyquinone being formed, from which a hydroxyquinone is set free on addition of an acid. It is a light red, crystalline powder, which melts at about 186—187°, readily soluble in alcohol, benzene, glacial acetic acid, and ethyl acetate, and its composition and molecular weight show that it is derived from the quinone by the replacement of a hydrogen atom by a hydroxyl group. This compound, when dissolved in a hot solution of potassium hydroxide and oxidised by a solution of potassium permanganate, yields phthalic acid, carbon dioxide, and β-naphthoic acid.

This seems to show that the quinone is really β-naphthyl naphthoquinone, $C_{10}H_5{\cdot}O{\cdot}C_{10}H_7{\cdot}O$ (1 . 2 . 4), the replacement of hydrogen by hydroxyl and the breaking down of the molecule taking place as follows.



The second quinone, $C_{20}H_{10}O_4$, is produced in small quantity if a considerable excess of chromic acid is used in the oxidation and if the action is prolonged. It can easily be separated from β-naphthyl-naphthoquinone by its slight solubility in alcohol. It is probably formed by the further oxidation of the naphthyl naphthoquinone, as it is always accompanied by more or less of that substance and by tarry decomposition products.

The quinone, $C_{20}H_{10}O_4$, is a light brown, somewhat earthy-looking powder, the particles having no definite crystalline shape. It is moderately soluble in boiling glacial acetic acid and benzene, slightly in hot alcohol. It melts at about 216—217°, and gives a deep orange colour with cold concentrated sulphuric acid. It behaves very much like the simpler quinone, its behaviour being modified apparently by its containing two naphthoquinone groups instead of one. When heated with a solution of potassium hydroxide, it is dissolved, forming a dipotassium derivative, the liberated hydrogen, as before, reducing the quinone, $C_{20}H_{10}O_4 + 2KOH = C_{20}H_8(OH)_4(OK)_2$. In presence of air, the hydroxyl groups are oxidised, and, on addition of an acid, a dihydroxydiquinone of the composition $C_{20}H_8O_4(OH)_2$, is thrown down. This forms a dark red, almost black, powder, which gives a red streak on unglazed porcelain. It melts near 215°, and is easily soluble in glacial acetic acid, ethyl acetate, and alcohol. When dissolved in a boiling solution of potassium hydroxide and oxidised by a solution of potassium permanganate, it yields apparently only phthalic acid and carbon dioxide, which makes it probable that the quinone is ββ-di-α-naphthoquinone, $C_{10}H_5O_2{\cdot}C_{10}H_5O_2$ (1 . 2 . 4 . 1 . 2 . 4), the actions being represented as follows.

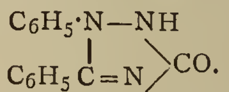


77. "*Action of Benzaldehyde on Phenylsemicarbazide.*" By George Young, Ph.D.

When alcoholic solutions of benzaldehyde and phenylsemicarbazide are evaporated to dryness, reaction occurs according to the equation—

$$C_7H_9N_3O + C_7H_6O + O = C_{14}H_{11}N_3O + 2H_2O.$$

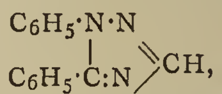
The yield is much increased by adding an oxidising agent such as ferric chloride. The product, which has slight basic and decided acid properties, is a diphenyloxytriazol,



$$\begin{matrix} C_6H_5{\cdot}N-NH & \\ \quad | & \rangle CO. \\ C_6H_5\,C=N & \end{matrix}$$

The silver salt, $C_{14}H_{10}N_3OAg + H_2O$, and the hydrochloride, $C_{14}H_{11}N_3OHCl + 2H_2O$, have been prepared; the latter is dissociated by water. The acetyl derivative, $C_{14}H_{10}N_3O(C_2H_3O)$ (m. p. 133°) is prepared by the action of acetic anhydride and sodium acetate. The ethylic ether, $C_{14}H_{10}N_3O(C_2H_5)$ (m. p. 92°) is prepared by the action of ethyl iodide on the silver salt or by heating diphenyloxytriazol with potassium hydroxide, ethyl iodide, and ethyl alcohol for an hour in a sealed tube at 100°.

The diphenyloxytriazol is reduced to diphenyltriazol, a weak base—



$$\begin{matrix} C_6H_5{\cdot}N{\cdot}N & \\ \quad | & \rangle CH, \\ C_6H_5{\cdot}C{:}N & \end{matrix}$$

(m. p. 91°), by heating with phosphorus pentasulphide to 230—250°, for six hours; its hydrochloride—

$$C_{14}H_{11}N_3HCl + 2H_2O,$$

and its platinichloride, $(C_{14}H_{11}N_3HCl)_2PtCl_4 + 4H_2O$, are both dissociated by water. The latter on being heated to 180° loses besides its water of crystallisation 4 molecular proportions of hydrochloric acid.

78. "*Note on the Latent Heat of Fusion.*" By N. F. Deerr.

If, in Mr. Crompton's relation (*Trans.*, cxlv., 240), $Aw/Tv = C$, $1/S$ where S is the specific heat, be substituted for A, we obtain $w/STv = C$, and when the valency is constant, $w/ST = C$.

In order that this relation may have a definite meaning, w/S must be temperature, or, symbolically, $w/S = T'$.

Then $w = ST'$, which, since w is quantity of heat, as is also ST', is a true relation. For the quantity w/S I would propose the term "temperature equivalent of latent heat of fusion," so that Mr. Crompton's relation may be expressed :—"When the valency of any series of elements is the same, the temperature equivalent of the latent heat of fusion bears a constant ratio to the absolute temperature of the melting point.

Denoting the temperature equivalent of the latent heat of fusion by T_f, and temperature of the melting point by T, the table below includes values of T/T_f for all the elements for which w is known; it will appear that there are exceptions to the rule, but that in the majority of cases the agreement is most striking.

Monads.

Elements.	T*f*.	T.	T/T*f*.
Sodium	111	365	3·32
Potassium	94	335	3·57
Silver	377	1220	3·25
Thallium..	167	565	3·35
Bromine	151	266	1·76
Iodine	217	386	1·78

Between the metallic elements considered separately, and also between the non-metallic elements, there is a remarkable agreement; it would not, however, be expected that there would be a law connecting elements with such widely varying properties as, say, bromine and sodium; it is, however, worthy of notice that the value of T/T*f* for bromine and iodine is very nearly half that for the metallic monad elements.

Dyads.

Elements.	T*f*.	T.	T/T*f*.
Zinc..	299	695	2·32
Cadmium	252	601	2·38
Mercury	90·5	233	2·58
Palladium	625	1700	2·72
Platinum..	875	2050	2·34
Lead	174	603	3·47
Tin	253	503	1·99

Lead and tin are taken as dyads: with the exception of the disagreement shown by these elements, the values of T/T*f* are quite satisfactory.

Triads.

Elements.	T*f*.	T.	T/T*f*.
Gallium	238	286	1·20
Phosphorus	25	317	12·05
Bismuth	434	535	1·23
Gold..	510	1328	2·60

The agreement between gallium and bismuth is satisfactory, and gold, although evidently triad, is better included with platinum and palladium; of the abnormal value of phosphorus I can give no explanation; it will be remembered, however, that in Mr. Crompton's relation the reciprocal of the valency was taken.

Tetrads.

Elements.	T*f*.	T.	T/T*f*.
Sulphur	57·5	385	6·70
Aluminium	133	870	6·55

Sulphur is taken as a tetrad, as it appears in the dioxide; the close agreement between sulphur and aluminium, perhaps, justifying this.

79. "*Acid Compounds of some Natural Yellow Colouring Matters.*" (Part I.). By A. G. Perkin and L. Pate.

In a previous communication by one of us (*Ber.*, xv., 2337) an account was given of some peculiar acid compounds formed by the action of mineral acids upon hæmatein and brazilein, the colouring matters of logwood and brazil-wood. In continuation of this work the behaviour of acids towards various natural yellow colouring matters has been studied, the results of which are embodied in the accompanying table.

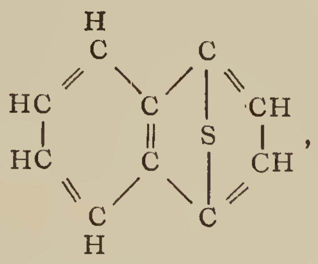
	H_2SO_4.	HBr.	HCl.	HI.
Quercetin	$C_{15}H_{10}O_7 \cdot H_2SO_4$	$C_{15}H_{10}O_7HBr$	$C_{15}H_{10}O_7HCl$	$C_{15}H_{10}O_7 \cdot HI$
Rhamnazin	$C_{17}H_{14}O_7 \cdot H_2SO_4$	No action	No action	No action
Rhamnetin	$C_{16}H_{12}O_7H_2SO_4$	,,	,,	,,
Luteolin	$X \cdot H_2SO_4$	,,	,,	,,
Fisetin	$C_{15}H_{10}O_6H_2SO_4$	$C_{15}H_{10}O_6HBr$	$C_{15}H_{10}O_6HCl$	
Morin	$C_{15}H_8O_6H_2SO_4$	$C_{15}H_{10}O_7HBr$	$C_{15}H_{10}O_7HCl$	$C_{15}H_{10}O_7 \cdot HI$
Catechin	No action	No action	No action	No action
Maceurin	,,	,,	,,	,,

These compounds are produced in the form of lustrous orange or scarlet needles, which cannot be re-crystallised without decomposition. On treatment with water they are decomposed into the original colouring matter and free acid, and a similar result occurs when the hydrochloric acid compounds are heated for some time to 100°.

As is well known the colouring matters here studied form two classes, only one of which combine with acids. Of these, fisetin and maceurin may be taken as types. A third class also exists in which are included gentisein, the colouring matter of gentian root (Tambor, "Inaug. Dissert, Leipsig, 1894") and datiscetin, which is obtained from *Datisca cannabina* (Schunck and Marchlewski, (*Annalen*, cclxxvii., 261).

80. "*Action of Sulphur on α-Nitronaphthalene.*" By A. Herzfelder, Ph.D.

When α-nitronaphthalene is heated at about 270° with 25 per cent of sulphur, vigorous interaction takes place, sulphur dioxide being evolued, whilst a black solid mass remains. From this solid an amorphous green substance was isolated which has the formula $C_{10}H_6S$, and the molecular weight 158. It dissolves in the same solvents as sulphur and melts at 155°, with decomposition. It possesses none of the properties of a mercaptan, and gives, on treatment with bromine, αα′-dibromonaphthalene. Its formula it most probably—



and the name αα′-thionaphthalene is proposed for it. The products of bromination, nitration, and sulphonation have been examined.

NOTICES OF BOOKS.

Explosives Act, 1875 (38 *Vict.*, *c.* 17). *Nineteenth Annual Report of Her Majesty's Inspectors of Explosives*; being their Annual Report for the Year 1894. London: Her Majesty's Stationery Office.

This report contains matter both of a highly satisfactory and of an alarming nature. As regards the working of the Act no objection can be raised. The total death rate from fire or explosion in manufacture has been reduced to 2, whilst the average for the previous ten years has been 4·6. This improvement has taken place in face of the fact that the number of factories and that of persons employed has decidedly increased, and that in many cases new explosives are being manufactured the risks of which are less well known. The number of factories has risen from 55 (when the Act came into operation) to 130, and that of magazines from 199 to 380. Complaints as to the working of the Act are now becoming very rare, partly in consequence of the fact that foreign countries are introducing laws and regulations concerning explosives greatly based on the British model, but, as a rule, much more stringent.

During the year, four factories have become extinct; seven new factories have been licensed; six applications for new licenses have been received during the year, and there are eight applications outstanding from the previous year.

The growth of the trade since 1875 has been very remarkable.

The following explosives have been added to the authorised list:—Blasting amberite, cordite, collodion cotton, westfalite, von Forster's powder. Compositions containing sulphur in conjunction with chlorate.

The arrangements adopted by the German government for marking all cartridges, so as in case of accidents to identify their origin, have not been adopted, since, though elaborate and costly, the precautions could easily be defeated. But devices for identifying all packages of explosives have been already partially adopted. During the year 192 visits have been made to the factories and infractions or evasions of the Act have been found very rare.

Only one instance has occurred of unlawful entry into a factory and theft of explosives. One instance has occurred of illegal manufacture—blasting cartridges.

In floating magazines additional precautions are recommended. One magazine, at Sancreed, has been struck by lightning, but damage was prevented by the conductor, though the ground was torn up round the earth plates, showing that the resistance to earth was too high. Occasional inspection by a competent electrician is suggested.

The doors of stores for explosives are now very generally protected by iron plating. At the Bryncethin Slate Quarry 4 lbs. of dynamite, 1 lb. of powder, and 16 yards of safety fuse were stolen.

A vessel conveying 20,000 lbs. of dynamite and 10,500 lbs. of blasting gelatin was totally wrecked on rocks at Holy Island; the cargo "was scattered about the rocks and in the water." Steps were immediately taken for its collection and destruction, since there is no reasonable limit to the time during which danger may continue. In a former case at Larn two men were killed by the explosion of some nitro-glycerin remaining from the wreck of the *Essequibo*, nine years previously.

According to the results of a special investigation by Dr. Dupré, re-dipping gun-cotton in fresh acids is a dangerous operation.

The gunpowder explosion on December 13, 1893, at the Waltham Abbey works, has been made the subject of a very careful investigation. The Committee decided that there were very grave defects in the system of discipline and precautions prevailing at Waltham Abbey, and that there is urgent necessity for a comprehensive revision of the regulations, and the adoption of disciplinary measures for their more rigorous enforcement." Of these defects the Committee specify twelve, but they do not wish to regard their list as exhaustive.

A second explosion ensued at Waltham Abbey, May 7, 1894, in connection with the preparation of cordite. There does not appear to have been any defect in the manufacture of the cordite, or of the nitro-glycerin and gun-cotton used as its ingredients. Nor does it appear that the calamity was in any way due to malice.

Accidents have happened with celluloid (xylonite, &c.), but the Inspectors do not see adequate reason for its inclusion in the list of dangerous substances.

There is a list of "scares, and hoaxes, and false alarms." We submit, however, that a part at least of these attempts may have been made in order to lull the authorities and the public into a feeling of false security from which they may some day be fearfully aroused. In one case, at least, the verdict of not guilty returned in the case of an anarchist—an alien—seems to us scarcely justifiable.

Two hoaxers, however, have been each fined £48, which will probably teach them to select other subjects for their jokes.

Meantime genuine outrages have not been entirely wanting. The Greenwich Park accident, of February 18, fortunately avenged itself on its would-be perpetrator, Martin Bourdin. In the case of the attempt against Burwell Church the evidence was insufficient, and as regards the bomb placed at one of the windows of a club at Yarmouth, the perpetrator was never detected.

Two avowed anarchists, Giuseppe Farnara and Polti, were convicted and received the sentences of respectively twenty and ten years penal servitude.

Other attempts were also made concerning the *animus* of which no rational doubt can exist,

Foreign outrages have been more numerous and more deadly, especially in the United States, where, however, much of the mischief seems to have been due to European immigrants. France, Spain, Austria, Italy, and Belgium have been by no means free from the spirit of murderous outrage. In most countries stringent laws have been enacted for the repression of anarchism. It is interesting to learn that the French explosive, mellinite, has still not become exactly known. We may venture to say that had a secret deemed of such national importance been in British hands its composition, with all working details, would ere this have become known to those governments with which there is any possibility of our being involved in war.

Appendices give a table of factories, with a list of the explosives authorised to be made there; a table of explosives authorised to be made in Britain; list of explosives which have passed the tests, but for which no licenses have as yet been taken out; the distribution in counties of factories, magazines, and toy firework factories; also of stores and registered premises; the Order in Council prohibiting fireworks containing sulphur in admixture with chlorates; list of railways whose by-laws have been confirmed; total amount of explosives imported; quantity and value of home-made gunpowder exported.

A special appendix contains a list of the more important outrages and attempts from 1881 to 1894.

CORRESPONDENCE.

"STEEL WORKS ANALYSIS."

To the Editor of the Chemical News.

Sir,—I am sorry that I must beg a little space to reply to Prof. Arnold's letter (Chemical News, vol. lxxi., p. 292). I had decided to pay no attention to Prof. Arnold's criticism in his new work, but a few weeks ago there appeared in a special and important number of the *Iron and Coal Trades' Review* a specially contributed article in which it is stated that "Prof. Arnold, by a modification of Galbraith's volumetric method, obtains reliable results in testing steels for chromium."

Of course, I have no right to ask who wrote the article, but my letter, which also appeared in that journal, has so far elicited no reply.

In his letter he repeats the necessity of diluting the solution. His fears here are contrary to my own experience and to any literature there is on the subject.

He mentions now, however, another objection—"That the large manganese precipitate carries down some chromium with it." Well, we have known that for a long time, but I thought Mr. Stead and I were the first to point that out, in the papers referred to, in the year 1893, and in order to deal with this, I described two remedies —indeed, this was the sole reason of Mr. Stead's modification, and of the precautions mentioned by me; and as the whole teaching of these papers was that there was no fear of non-oxidation of the chromium oxide, it was not difficult to see the unwisdom of using a large excess. But Mr. Stead specially mentions this in his paper of May, 1893. He says: "These results clearly show that the amount of permanganate requires to be carefully regulated," &c.

I do not know to what meeting of two or three years ago Prof. Arnold refers to, where he described a modification in my presence; I was certainly not present at such a meeting. But why did he condemn it in the spring of 1893 if two or three years ago he modified it?

I will not, however, pursue the question further, because if Prof. Arnold remembered "a florid denunciation" of his process by me, and that I declared his process "gave results 50 per cent too high," I can understand his criticisms and have some sympathy with them. I am quite sure, however, if he will make enquiry of those who were present and try to remember what took place, he will acquit me of this.

I did not at the meeting referred to, nor have I at any time, criticised it in any way whatever. Indeed, I had never even tried it; I do not mean by that that I have any opinion about it one way or another. I was simply engaged in the defence of my own method.—I am, &c.,

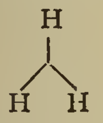
Wm. Galbraith.

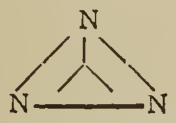
Chesterfield, June 21, 1895.

DIAGRAMMATIC FORMULÆ.

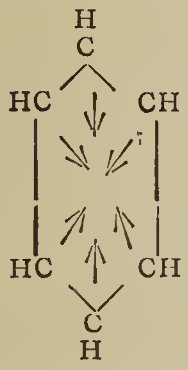
To the Editor of the Chemical News.

Sir,—May I venture to protest against the use of such formulæ as Dr. Brauner proposes for condensed hydrogen and nitrogen, viz.:—





These formulæ, in common with Baeyer's formula for benzene—



are extremely objectionable, inasmuch as they tend to produce a state of mental satisfaction which has no real foundation. Such pseudo-explanatory diagrams are an abuse of graphic formulæ, the legitimate use of which is to connote the chemical—and to some extent the physical—properties of the substances which they are intended to represent. Students are especially liable to be led astray by formulæ like these, which on closs examination are found to be perfectly meaningless.—I am, &c.,

L. Parry, A.R.S.M.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Academie des Sciences. Vol. cxx., No. 23, June 10, 1895.

Spectroscopic Examination of the Carbons of the Electric Furnace.—H. Deslandres.—Will be inserted in full.

Physical Properties of Acetylene: Acetylene Hydrate.—P. Villard.—Acetylene is solidified by evaporation in the open air. Its melting-point is −81°. The crystals of solid acetylene, like those of carbonic acid, are absolutely without action upon polarised light. The solubility of the gas has been determined at 0° under the pressure of 4·65 atmospheres. Under these conditions the coefficient of solubility is = 1·6. Acetylene hydrate was first observed by Cailletet in 1871. It is denser than water, and its crystals have no action on polarised light. Its composition may be represented by the formula $C_2H_2,6H_2O$.

Synthetic Formation of Nitro-alcohols.—Louis Henry.—Not adapted for abridgment, and scarcely of sufficient importance for insertion *in extenso*.

Condensation of the Aldehyds and the Saturated Acetones.—Ph. Barbier and L. Bouveault.—From these researches it seems established that among all the acetones, ordinary acetone alone condenses easily with the aldehyds. When the molecular weight of the aldehyds increases, their aptitude for condensation with acetone diminishes, and the chief reaction becomes the condensation of the aldehyd itself.

Causes of the Colouration and of the Coagulation of Milk by Heat.—P. Cazeneuve and M. Haddon.—The yellow colouration of milk on exposure to heat is due to the oxidation of the lactose in presence of the alkaline salts of the milk. Lactose during this oxidation yields acids, especially formic acid, easily detected, the presence of which suffices to explain the coagulation of the milk, as it ensues with any acid. The caseine coagulated is not modified under these conditions, but is merely tinged yellow by brown substances formed at the expense of the lactose.

Active Ethers of the α-Oxybutyric Acids.—Ph. A. Guye and Ch. Jordan.—The authors classify these ethers in five series, and tabulate their optical properties.

Alkaloids of the Fumariaceæ and Papaveraceæ.—M. Battandier.—*Bocconia frutescens* yields fumarine identical with that of *fumaria*, and another alkaloid which is turned to a peach-colour on contact with sulphuric acid, and which he proposes to call "bocconine," traces of a third base having reactions very similar to those of chelidonine, and, lastly, abundance of chelerythrine. Fumarine may occasion an error in the toxicological search for strychnine. The glaucine of Probst contains small quantities of fumarine which gives it the property of taking a violet colour in the cold on contact with sulphuric acid.

A Contribution to the Study of Germination.—Th. Schlœsing, jun.—The author concludes from his experiments that the germination of the grain of wheat and of lupins does not involve any appreciable loss of nitrogen in a gaseous state.

On Amylase.—M. Effront.—An infusion of barley, made in the cold, and then filtered and boiled, triples, and even quintuples, the diastasic power of malt. The value of two malts is proportional to the ratio existing between their saccharifying and liquefying powers.

Employment and the Modus operandi of Chloride of Lime against the Bite of Venomous Serpents.—C. Phisalix and G. Bertrand.—All the experiments of the authors concur in demonstrating that the solution of chloride of lime, advocated against the bite of venomous serpents, has only a local action. It destroys the venom and modifies the tissues, thus obstructing the absorption of the toxic matter. Injections of chloride of lime made at other points than that of the bite have no immunising power, and must be avoided. It is necessary to inject deeply at the very part where the fangs have penetrated.

Revue Universelle des Mines et de la Metallurgie. Vol. xxx., No. 1.

This issue contains no chemical matter.

MISCELLANEOUS.

Study on the Values of the most usual Methods for the Determination of Carbon in Iron. — H. Ledebur. — This extensive paper cannot be reproduced without the six accompanying figures. The author concludes that the two gravimetric methods of Särnström for the determination of the total carbon are the most usual and the most advantageous for use in the metallurgical laboratory.—*Bull. Soc. d'Enc. l'Ind. Nationale*, x., No. 111.

Inspectorship of Alkali Works. — An interesting event took place on the 31st ult., in connection with the retirement of Mr. Alfred E. Fletcher, F.I.C., from the Chief Inspectorship of Alkali, &c., Works, a post which he had held for eleven years. Mr. Fletcher was one of the original Inspectors appointed under the first Alkali Act of 1863, being the only one remaining in office of the original five officials then appointed. Mr. Fletcher was entertained by the Staff at dinner, held at the Hotel Previtali, when presentation was made to him, by his late colleagues, of a silver Monteith bowl with a suitable inscription. Mr. R. Forbes Carpenter, F.I.C., has been appointed by the Local Government Board to succeed Mr. Fletcher as Chief Inspector. Mr. Carpenter joined the Staff in 1882, having subsequently been in charge of the East Lancashire and Yorkshire District.

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END OF VOLUME LXXI.